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"Energetic Oxetane Thermoplastic Elastomer Binders"

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ABSTRACT

Energetic oxetane-based (AB)_n block copolymers have been prepared that are the first examples of this class of materials that exhibit true elastomeric properties (greater than 100 percent recoverable strain). The materials are prepared by separately synthesizing the A and B blocks as hydroxyl-terminated telechelic prepolymers then linking the materials using optimized isocyanate chemistry. The individual blocks are prepared using the activated monomer polymerization which allows careful control of molecular weight and functionality. A large number of various hard and soft block combinations were prepared. The hard block was always a poly(3,3-bis(azidomethyl)oxetane) (BAMO) and a series of soft blocks were examined which were based on 3-azidomethyl-3-methyloxetane (AMMO), 3-nitratomethyl-3-methyloxetane (NMMO) and random copolymers of these two monomers with BAMO. Chemical and mechanical measurements on the block copolymers prepared showed that BAMO-AMMO (AB)_n materials exhibited the best overall properties. Initial materials exhibited unacceptably high melt viscosities but minor changes to the linking reaction afforded materials with much lower melt viscosities. These materials were mixed with bimodal AP and with bimodal CL-20 at a 65 percent solids loading. Mechanical properties were encouraging. Later mixes replaced 15 percent of the polymer with aluminum to afford an 80 percent solids propellant with encouraging mechanical properties. All mixes were prepared in a small vertical mixer and processed at roughly 95° C.

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SUMMARY

An attractive approach to high energy propellants involves the use of energetic oxetane thermoplastic elastomers (TPEs). Theoretical performance calculations on energetic oxetanes using experimental heats of formation have shown an increase of 8 lb-sec/lb relative to a PEG baseline in a minimum smoke propellant and no loss in Isp while dropping from 91% solids to 75% solids in an AP/Al formulation by replacing HTPB. TPEs as a class of propellant binders are attractive from a processing point of view in terms of lower cost and increased safety. However, no viable oxetane TPE propellant binders had been prepared before this program and, in fact, no firm reports of any oxetane block polymers that meet the firm technical definition of a TPE (thermally processible with greater than 100% recoverable strain) existed either. Therefore, the projected payoffs have not been realized. Our approach to this problem was to investigate an alternative polymerization of energetic oxetanes that we have shown has distinct advantages over the methods previously used. This chemistry serves as the basis for a sequential polymerization to form ABA block copolymers and for isocyanate linking to form ABA and (AB)_n block copolymers. This improved chemistry has allowed the attainment of the goal to developing a viable oxetane TPE propellant binder.

RESULTS AND DISCUSSION

The first report¹ in the literature of the unambiguous synthesis of an oxetane containing block polymer by a direct polymerization method suggests the difficulties to be encountered in the preparation of these materials. Ample evidence exists from research into the preparation of energetic oxetane block polymers to suggest that similar difficulties are to be found with these materials also. Years of SDIO/IST sponsored work at Thiokol, NAWC and Aerojet had failed to provide oxetane-based TPEs with the desired high strain, high stress and low modulus required for the preparation of propellant with acceptable mechanical properties.

A chemical linking of previously prepared telechelic homopolymers is an alternate approach to the synthesis of block polymers. This is the approach used^{2,3} to prepare oxetane-based (AB)_n block materials for LOVA

gun propellant binders. These binders have a high melt viscosity which is consistent with the gun propellant formulation which is extruded as a seven perforation grain. An obvious extension of this work was into the synthesis of ABA- or (AB)_n-type materials tailored for solid rocket propellants as envisioned on this SDIO/IST-ONR program. This approach to block copolymer materials has the distinct advantage of utilizing a fully developed chemical strategy and proven analytical techniques. The missing factor in the effort was a consistent, controllable polymerization of oxetane blocks for the chemical linking. Much of the work done on the gun propellant program utilized purely empirical methods to obtain desirable block make-up. Consistent results were difficult to obtain. This problem was a fundamental roadblock to the program and required a solution.

An approach to the polymerization problem, suggested by work performed on epichlorohydrin,⁴ was explored. After our work was underway, a similar approach was reported to be effective in preparing a monofunctional polymer of 3-methyl-3-(trimethylsiloxymethyl)oxetane.⁵ This approach involves altering the mechanism from a polymerization involving a cation in the growing chain to the attack of a hydroxyl-terminated polymer on an activated monomer (Figure 1). This type of polymerization is obviously

Standard Polymerization:



Activated Monomer Polymerization:

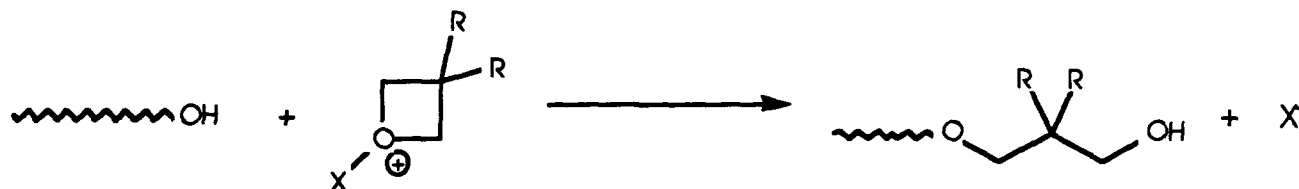


Figure 1. Depicted in this figure is the proposed mechanism for the propagation step of oxetane polymerization by the standard method and by the activated monomer method. The key difference is the activated monomer method involves attack of an alcohol on an activated monomer, which ensures rapid and complete initiator incorporation into the polymer chain.

not a classical cationic mechanism. Several examples of this type of polymerization have been shown^{4,5} to approximate many of the characteristics of a living polymerization. To such a polymerization, the term "pseudo-living" is often applied. As a result of ongoing research with this system, reaction conditions have been developed that allow a controlled polymerization of energetic oxetanes with high initiator incorporation (which dictates functionality) and good molecular weight control. This has resulted in the production of true monofunctional energetic oxetane polymers. Besides monofunctional materials, di, tri and tetrafunctional materials are prepared with good control by this method (Figure 2). These data (Figure 2) are particularly significant because they show not only functionality control, but also the excellent molecular weight control attained. This degree of molecular weight control is necessary for the preparation of a series of block copolymers with controlled variation of total molecular weight and relative amounts of the individual blocks for mechanical property optimization and correlation to propellant properties.

The initiator system has been shown experimentally to exhibit the characteristics of an activated monomer "pseudo-living" polymerization mechanism mentioned above. This was shown by a series of classical tests of whether a polymerization is "living" involving the correlation of polymer properties and degree of conversion in the polymerization. These experiments illustrate the dramatic difference between oxetane polymerizations carried out using the activated monomer method and the earlier, standard method.^{6,7,8} In representative polymerizations to prepare difunctional 3,3-bis(azidomethyl)oxetane (BAMO) and 3,3-bis(ethoxymethyl)oxetane polymers using this activated monomer method and the earlier method, small aliquots were removed and quenched at several stages of the polymerization. The resulting polymers were analyzed,⁹ and the data gave a profile of the progression of the reaction (Figures 3 and 4). The molecular weight was shown to rise rapidly in the standard reaction and remain relatively constant throughout the polymerization typically with a small drop in the average molecular weight at high conversion. This drop in the molecular weight at the end of the reaction could be ascribed to attack of an active chain on an ether linkage of an existing polymer chain forming a tris(neoalkyl)oxonium ion

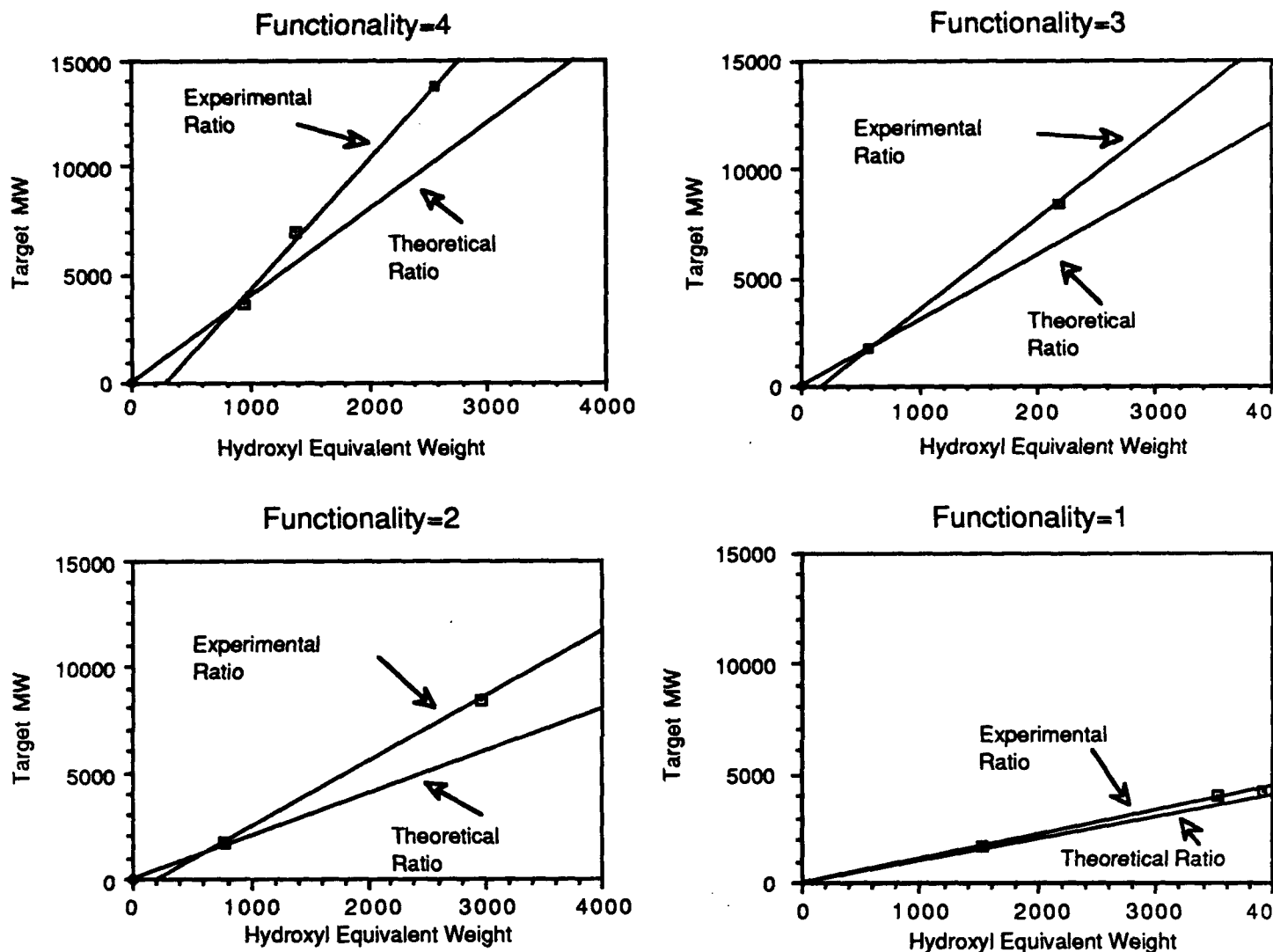


Figure 2. The series of graphs here details the success of the activated monomer polymerization at obtaining functionality and molecular weight control as evidenced by the close correlation of theoretical and experimental lines for molecular weight and experimental hydroxyl equivalent weight.

which results in chain scission on quenching. Alternatively, monomer starvation at high conversion could make termination reactions other than that mentioned above kinetically more competitive with propagation reactions than early in the polymerization. This would result in the production of lower molecular weight polymer at high conversion than at low conversion and, thereby, lowering the average molecular weight near the end of the reaction. In contrast, the activated monomer

polymerization showed a linear increase in molecular weight with conversion (Figures 3 and 4) with a Y-intercept near the origin. These are two classical characteristics of a "living" polymerization. Determination

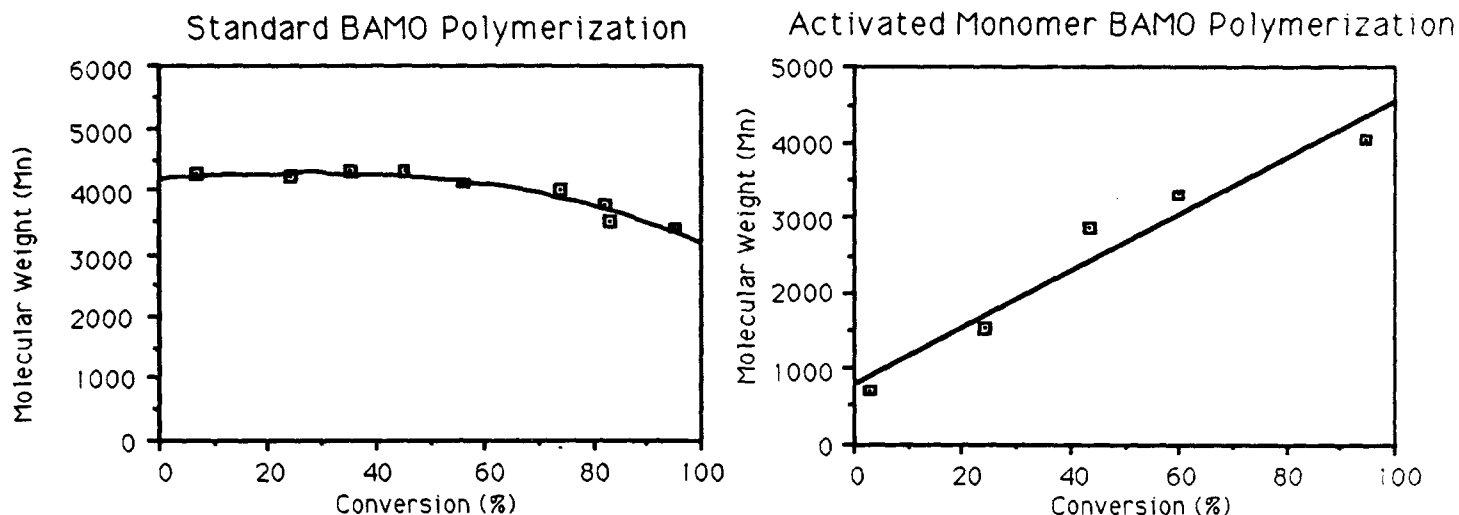


Figure 3. These two graphs illustrate the differences in the progress of BAMO polymerizations when carried out using the activated monomer method. The activated monomer method gives a linear increase in molecular weight with a Y-intercept near the origin, two key characteristics of a living polymerization.

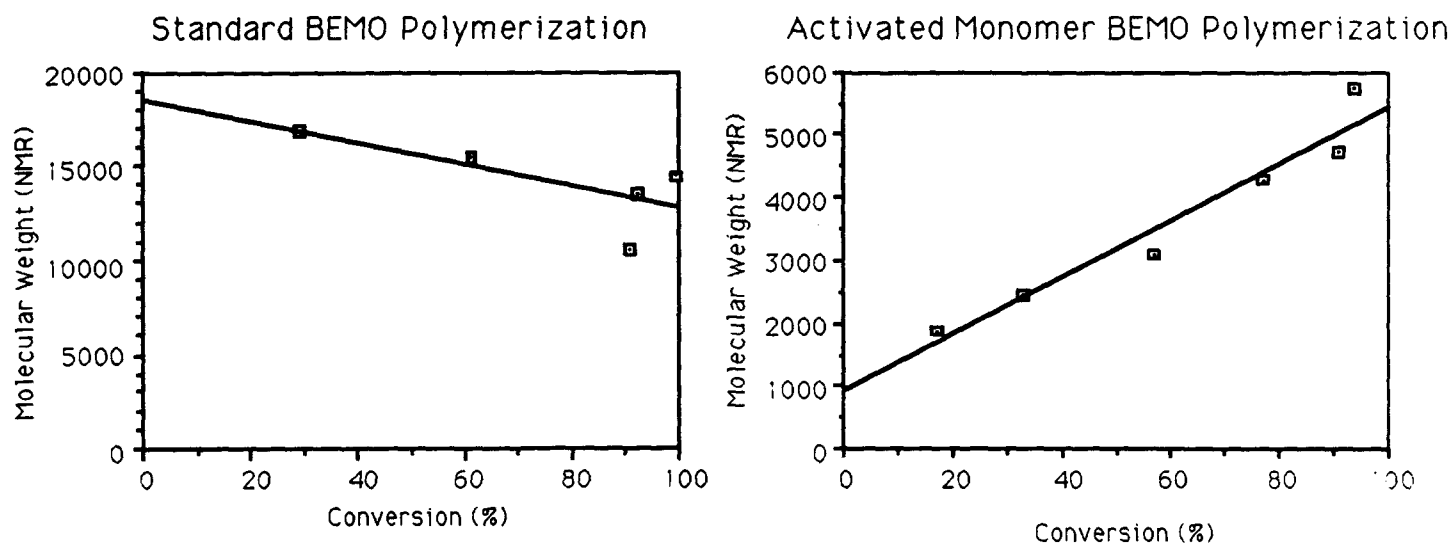


Figure 4. The two graphs above illustrate the difference in the progress of BEMO polymerizations when carried out using the activated monomer method. The activated monomer method gives a linear increase in molecular weight with a Y-intercept near the origin, two key characteristics of a living polymerization.

of the fate of the initial alcohol initiator charge also serves to highlight the differences in these two polymerizations. In the activated monomer polymerization, the initiator is incorporated into the polymer to a high degree early in the reaction with the majority ultimately incorporated internally (i.e. both alcohol moieties of a butanediol have functioned as initiating sites). The standard polymerization resulted in a low degree of initiator incorporation (Figures 5 and 6). These data also support the claim that the modified activated monomer polymerization is "pseudo-living." Further support for the mechanisms proposed (Figure 1) is a reduction of oligomeric products in the modified polymerization relative to the standard polymerization. Similar data, not shown in the figures reproduced here, have been obtained for polymerizations involving 3,3-dimethyloxetane.

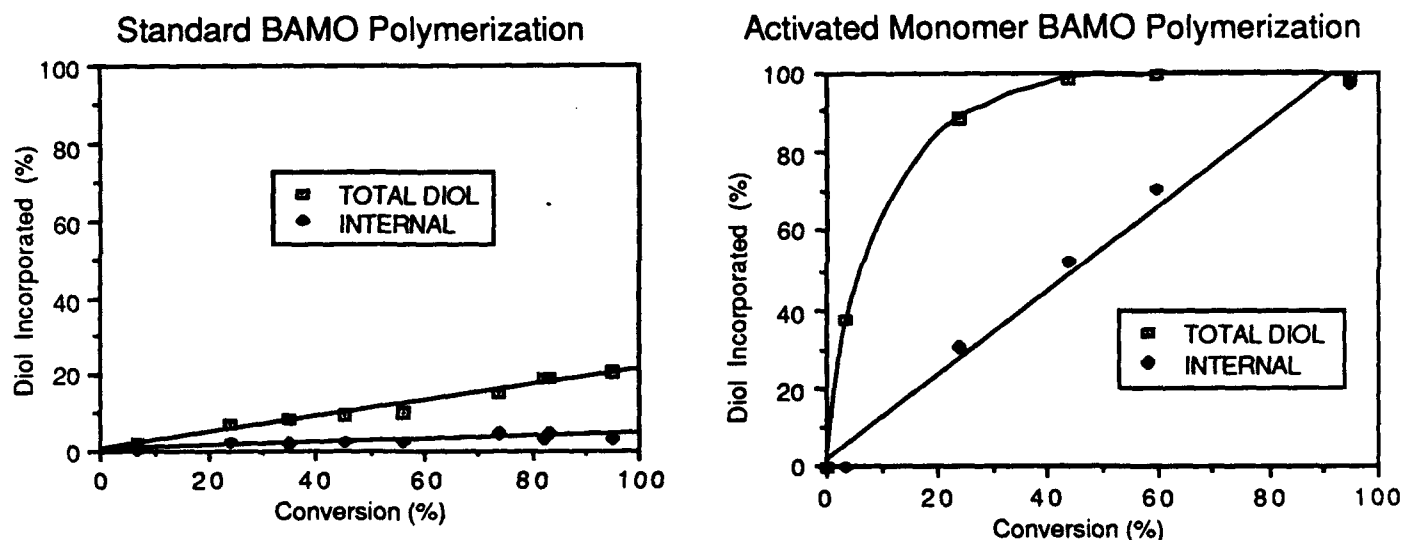


Figure 5. The two graphs above show the dramatic difference in the initiator incorporation for a BAMO polymer under the activated monomer reaction conditions. These data are in line with the mechanistic discussion and show the dramatic improvement made by this approach.

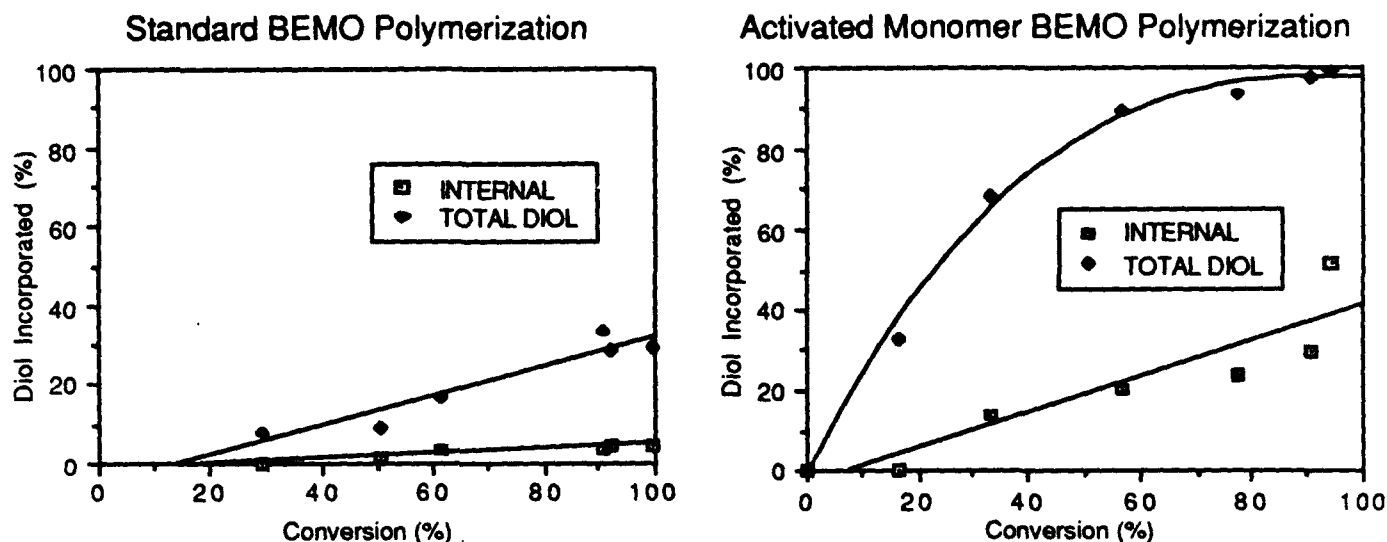


Figure 6. The two graphs show the dramatic difference in the initiator incorporation for a BEMO polymer under the activated monomer reaction conditions. These data are in line with the predictions based on the mechanistic discussion and show the dramatic improvement made by this approach.

These data suggested that the preparation of a bona fide oxetane ABA block copolymer by a sequential polymerization may in fact be possible using this "pseudo-living" polymerization. In a typical attempt to form an ABA block copolymer sequentially, a difunctional polymerization of 3-(azidomethyl)-3-methyloxetane (AMMO) was allowed to proceed to completion. At that time, a small aliquot of that reaction was removed and analyzed so that information on the intermediate AMMO homopolymer would be available for comparison to the final copolymer. A second charge of monomer was then added which, in this case, was BAMO. After the BAMO was polymerized the reaction was quenched and the product isolated. Using BAMO and AMMO monomers is particularly advantageous due to considerable data which has been generated on the analysis of resulting copolymers by ^{13}C and ^1H NMR.^{10,11,12} NMR methods alone are not sufficient to establish that a polymer has the desired ABA structure, however, they do provide information about several necessary conditions with a very rapid and simple experiment. Data from a representative attempt at the preparation of an ABA material by this reaction are given in Table I. A similar material was submitted to NAWC for their detailed analysis.¹³ Results from the GPC fractionation of that material are given in Figure 7.

TABLE I.
Representative Results from the Preparation of an ABA Material
by a Sequential Polymerization Using the Thiokol Activated Monomer
Method^a

Sample Ref	Ratio (AMMO/BAMO)	Mw	Mn	Disp	NMR MW	Endgroups (AMMO/BAMO)	Block Factor	Block Index	Hydr Eq Wt
7290	100/0	4.1	2.5	1.67	3.4	100/0	0	100	1689
7293	52/48	6.8	4.1	1.66	7.4	20/80	22	94	3247
Theory	50/50	--	--	--	7.4	0/100	21	92	3688

^aMw, Mn and NMR MW are given in thousands. The block factor is as has been defined⁵ which is the difference between the fraction of triads resulting from BAMO-BAMO-BAMO and BAMO-BAMO-AMMO, as measured by the fully relaxed ¹³C NMR of the quaternary carbons in the polymer, divided by 2. The block index is the sum of the integration of the absorbencies of all BAMO-BAMO-BAMO triads and AMMO-AMMO-AMMO triads divided by the total number of triads. These data show the effective formation of a block material and that the second monomer was polymerized without an increase in polydispersity. The endgroup data shows that the material contains 60-80% of the desired ABA structure.

These data show that several necessary conditions for an ABA structure were met. The ¹H NMR spectrum most directly shows the deviation of the properties of the material obtained from that desired. The data in Table I are interpreted to require, if all the AMMO endgroups are assumed to be related to homopolymer, that 80% of the product has the desired ABA architecture. Alternatively, if the assumption is made that all AMMO endgroups are related to a diblock material, then only 60% of the product has the desired ABA structure with the remaining 40% being diblock. Most likely, chemical reality is somewhere in between, although the lack of an increase in polydispersity on polymerization of the second monomer relative to that obtained for the homopolymer suggests that the diblock structure is the predominate impurity. The GPC fractionation data also support the theory that the diblock is the likely impurity. To date, the best efforts have provided slightly higher percentages of BAMO hydroxyl endgroups than those listed in Table I. The data indicate that, at best 85% of the product has the ABA arrangement (assuming homo AMMO as the other product). Although this percentage is relatively high and comparable to several commercial ABA materials, an unambiguous route to high purity ABA materials by a sequential polymerization is still under investigation.

GPC FRACTIONATION OF SEQUENTIALLY POLYMERIZED BAMO-AMMO-BAMO

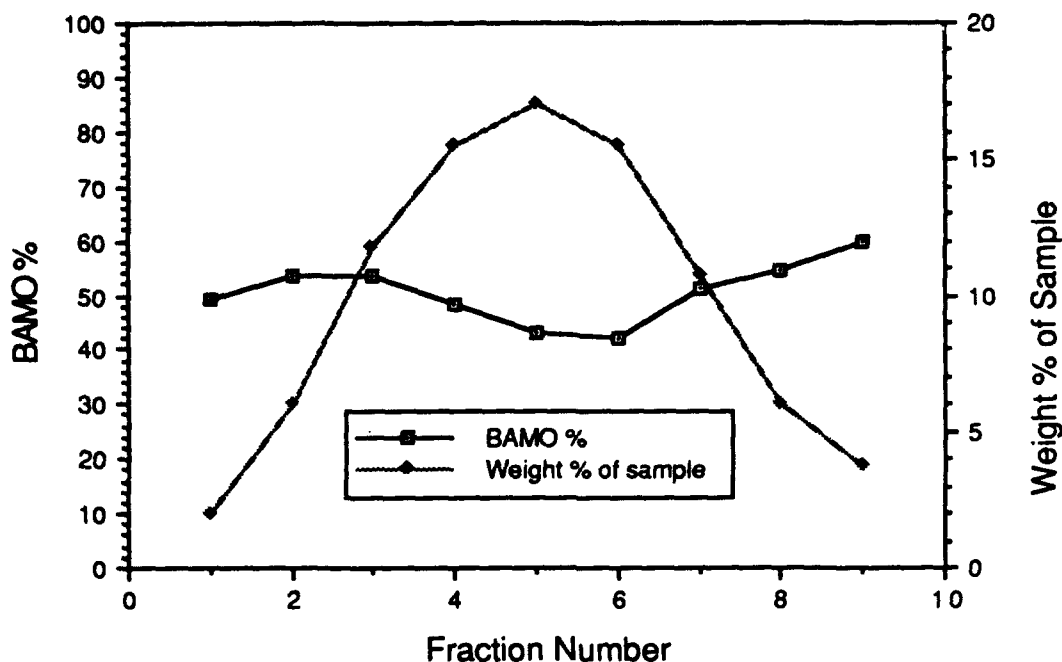


Figure 7. Reproduced here are the data obtained at NAWC from quantitative GPC fractionation of a Thiokol activated monomer polymerized BAMO-AMMO-BAMO block copolymer. These results show a consistent percentage of BAMO throughout the entire molecular weight range of the polymer, suggesting good block copolymer formation.

The chemical answer given above does not address the practical question of whether the mechanical properties of block copolymers with the composition described above will be acceptable. Therefore, as proposed for this program, a series of oxetane ABA block copolymers were prepared with controlled properties (e.g. molecular weight, percent hard block) then structurally characterized here at Thiokol and in conjunction with NAWC. The emphasis was placed on a thorough understanding of the chemical roots of the physical characteristics of the polymer so that modifications to the chemistry are made that will result in significant improvements in the polymer. A lack of this understanding would lead to confusion and ineffective research. The catalyst work has centered on two catalysts ($\text{BF}_3\text{-OEt}_2$ and Et_3OBF_4). Modifications have been made in the polymerization guided by the results from the analysis of the polymers. The largest deviation from the desired structure noted initially was

ascribed to the presence of adventitious moisture in the reaction mixture despite normal laboratory efforts to exclude moisture. We changed our experimental procedure to avoid the moisture problem by using Schlenk techniques which are commonly employed in the preparation and use of highly moisture and oxygen sensitive organometallic (including polymerization catalysts) and inorganic compounds. These precautions have effectively eliminated the moisture problem. The limiting factor at this time is catalyst reactivity. The catalysts currently employed do not appear to be effective in preparing high molecular weight polymers ($>30,000$ molecular weight). A more active catalyst would be an obvious suggestion, but the more active catalysts we have examined to not exhibit enough stability under the reaction conditions to be viable candidates. Unfortunately the best sequentially prepared ABA materials have failed to produce a product with attractive mechanical properties, therefore, an alternate approach to an oxetane TPE was sought.

A chemical linking of previously prepared telechelic homopolymers is the approach used³ to prepare oxetane-based (AB)_n block materials which are thermoplastic elastomers on a recent Ballistics Research Laboratory sponsored program into the use of these oxetane copolymers as LOVA binders. Besides preparation of (AB)_n materials, an obvious extension of this work was an examination of the synthesis of ABA-type materials. This approach to ABA materials has the distinct advantage of utilizing a fully developed chemical strategy and proven analytical techniques. Any attempt to link difunctional A and B blocks and form exclusively ABA materials by controlling stoichiometry of the blocks is statistically unrealistic. To cleanly form an ABA thermoplastic elastomer material by a post polymerization linking, an absolutely monofunctional hard (A) block is needed. Our activated monomer polymerization has made monofunctional oxetane hard (A) block materials available and led directly to the unambiguous synthesis of ABA materials by a chemical linking with a difunctional soft (B) block. The preparation of an ABA material followed well precedented lines because the reaction could be performed in a fashion completely analogous to that used to prepare (AB)_n materials by a block linking approach.¹⁴ Generally, a monofunctional hard block, typically BAMO, is allowed to react with a slight molar excess of 2,4-toluenediisocyanate (2,4-TDI) in the presence of a catalytic amount of diphenyltin dichloride. The large differential reactivity of the two

isocyanate functionalities, estimated at a factor of 26.6 when reacting with an unhindered alcohol,¹⁵ precludes any measurable dimerization reaction from occurring. The resulting isocyanate terminated polymer is then allowed to react with a difunctional (or higher functionality) soft block such as AMMO or NMMO. The progress of the reaction is monitored by both 300 MHz ¹H NMR and FTIR. These two analytical methods complement and corroborate each other well in this instance. The progress of the isocyanate plus alcohol reaction to afford urethane can be followed easily. In ¹H NMR spectra, the methylene adjacent to the terminal alcohol has a signal distinct from that same methylene when adjacent to a urethane linkage. These two absorbences can be quantified and compared. The carbonyl absorbences of the isocyanate moieties in 2,4-TDI and in the urethane resulting from the condensation of these functional groups with oxetane terminal alcohols are well-defined and strong in an FTIR spectrum, even at the low concentration present in this reaction. This allows, parallel to monitoring of the alcohol-to-urethane reaction by ¹H NMR, the observation by FTIR of the conversion of the isocyanate to urethane based on carbonyl absorbences. Together these methods provide strong evidence that the intended block linking reaction is proceeding as intended. A set of typical NMR and FTIR data obtained during the linking of oxetane materials are given in Appendix A. Table II contains data obtained from the analysis of the product of a representative linking reaction which we have carried out.

TABLE II.
Representative Results from the Preparation of ABA Materials
by Block Linking^a

Sample Ref	Ratio (AMMO/BAMO)	Mw	GPC Mn	Disp	NMR MW	Endgroups (AMMO/BAMO)	Block Factor	Index	Hydr Eq Wt
18670	100/0	12.4	6.0	2.06	7.3	100/0	0	100	3546
18671	0/100	5.7	3.1	1.85	3.2	0/100	50	100	3521
05712	60/40	15.5	8.1	1.92	12.6	6/94	20	100	--
Theory	60/40	--	--	--	14.1	0/100	20	100	--

^aAll data are as defined in Table I. The BAMO 'endgroups' in the final product are the initiating alcohol used to prepare the monofunctional BAMO hard block. These data show that the reaction proceeds without a significant increase in polydispersity. Determination of the hydroxyl equivalent weight in the product by a titration method was not possible due to interference with the test method by the -NH- moieties of the urethane linkages.

As shown in Table II, the GPC molecular weight increased significantly while the polydispersity of the product is intermediate between the two starting materials. This shows that the linking reaction was largely successful and that side reactions were not significant. The ^1H NMR molecular weight and endgroup type are both based on the observation that nearly all the terminal alcohol groups were converted to urethanes leaving the pendant chain of the alcohol used to initiate the monofunctional polymerization of BAMO as the major endgroup. In the case of a block linking reaction, the ^{13}C NMR block data is somewhat trivial as the polymerizations were carried out separately so the existence of perfect block structure is to be expected. By this method, several materials have been prepared, although the $(\text{AB})_n$ materials have exhibited superior mechanical properties. Further evidence of the effectiveness of the linking reaction is given in figure 2. This figure shows data generated at NWC by a GPC fractionation of an $(\text{AB})_n$ material. The even percentage of BAMO content across the molecular weight range shows that a high percentage of the desired linking reactions took place.

In the course of the program, over one hundred lots of oxetane copolymers have been prepared with AMMO, NMMO, BAMO/AMMO or BAMO/NMMO soft (center) blocks and BAMO hard (end) blocks. The mechanical properties obtained are a significant improvement over previous materials (see Table III) and so the majority of current effort is centered in this area. The best data we have suggests that a gumstock should be rather low modulus with a high recoverable strain number and reasonable but not necessarily high stress to ultimately yield a "good" propellant. These materials seem to come closer to this desirable properties and away from the tough (higher modulus) leathery materials made in the past that have not shown good propellant properties. The conclusion from the mechanical property data shown is that the AMMO soft block materials have mechanical properties superior to the NMMO-based block copolymers. The BAMO/AMMO and BAMO/NMMO soft block materials similarly did not show the excellent properties the AMMO-based materials do. Ten copolymer and six homopolymer samples have been submitted to NWC for examination and four samples to CSD for rheological characterization. The samples sent to CSD showed that the $(\text{AB})_n$ materials prepared to date while exhibiting excellent mechanical properties did not melt and flow well.¹⁶ The high melt viscosity makes those materials unsuitable for processing into

propellant in a standard vertical mixer although extrusion is easily done with these polymers. The GPC fractionation data (figure 8) obtained at NAWC show that the (AB)_n structure has been achieved quite well.

TABLE III.
Representative Mechanical Properties Obtained from Oxetane Block Copolymers^a

<u>Type</u>	<u>Soft Block</u>	<u>Modulus (psi)</u>	<u>Strain (%)</u>	<u>Stress (psi)</u>
ABA-s	NMMO	642	12	32
ABA-s	NMMO	355	9	25
ABA-s	AMMO	146	24	19
ABA-I	AMMO	69	37	15
ABA-I	AMMO	319	72	57
ABA-I	AMMO	44	36	5
ABA-I	AMMO	106	76	37
(AB) _n	AMMO	76	64	18
(AB) _n	AMMO	86	282	71
(AB) _n	AMMO	187	74	46
(AB) _n	NMMO	235	33	36
(AB) _n	AMMO	149	228	74
(AB) _n	AMMO	101	189	62
(AB) _n	NMMO	346	60	48
(AB) _n	AMMO	170	65	44
(AB) _n	AMMO	290	306	117
(AB) _n	AMMO	260	138	75

^aType refers to the method of preparation of the block copolymer with ABA-s being sequentially polymerized ABA and ABA-I being an ABA material prepared by linking of preformed blocks. The soft block involved is as listed above. In all cases, BAMO was the hard block. Strain is true, uncorrected at maximum stress and stress is uncorrected. The dramatic improvement in mechanical properties in the (AB)_n materials is obvious.

In an effort to reduce the melt viscosity of these materials, minor adjustments were made to the amount of linking reagent used in the (AB)_n forming reaction which resulted in a material with lower viscosity but still excellent mechanical properties. The resulting TPE was processed at roughly 90°C in a vertical mixer and loaded up to 65 percent solids with both ammonium perchlorate and CL-20. The propellants formed each time had good integrity. Adding to successful processing was the use of GAP-plasticizer and low molecular weight BAMO homopolymer as processing aids. The complete formulation is given in Table IV. Ambient temperature

mechanical properties have been achieved with a modulus of 625 psi, uncorrected stress of 66 psi and 31% strain.

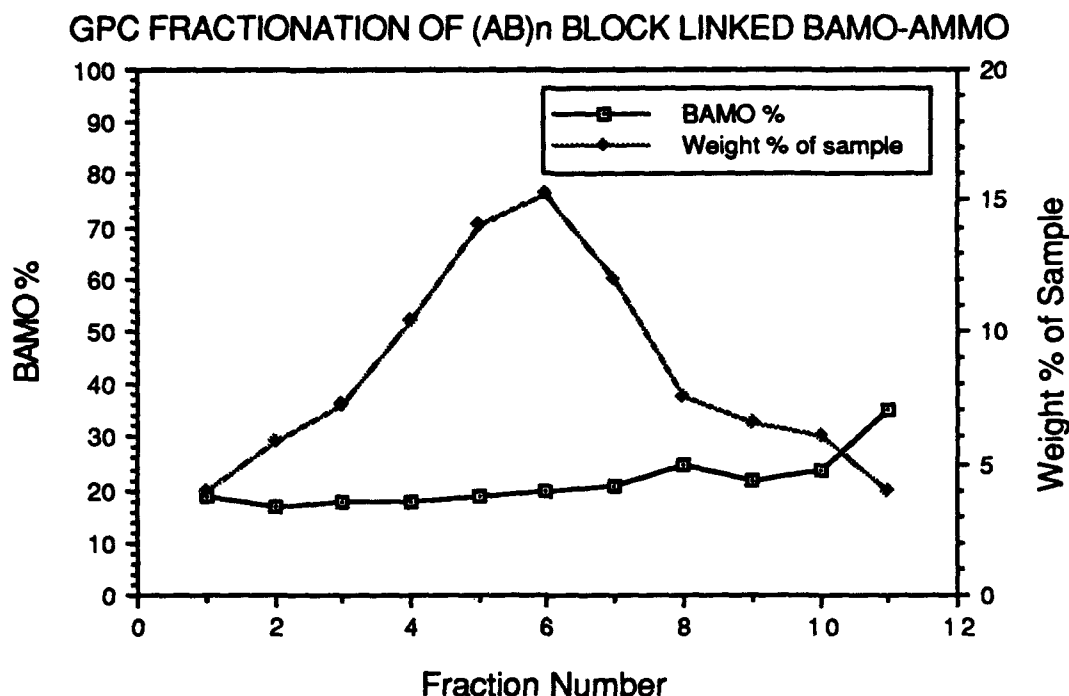


Figure 8. Reproduced here are the data obtained at NWC from quantitative GPC fractionation of a Thiokol (AB)_n block linked BAMO-AMMO copolymer. These results show a consistent percentage of BAMO throughout the entire molecular weight range of the polymer, suggesting good block copolymer formation.

CONCLUSIONS

The activated monomer approach to the preparation of oxetane polymers results in good molecular weight and functionality control. The polymerization has many of the characteristics of a living polymerization and can be used to prepare materials with a relatively high percentage of ABA block structure as desired. These improvements have led to the preparation of consistent, reproducible materials with improved properties as compared to previously prepared oxetane-based materials. While the ABA materials exhibited good molecular architecture, the mechanical properties were disappointing. Conversely, (AB)_n materials prepared by linking of individual blocks afforded excellent mechanical properties and, under carefully selected linking conditions, melt viscosity low enough for processing propellant based on this material in standard

vertical mixer. The resulting propellant exhibits mechanical properties considered acceptable for standard solid propellants.

TABLE IV.
Initial Propellant Mixes Processed in a Small 30-G Mixer

<u>INGREDIENT</u>	<u>MIX #1</u>	<u>MIX #2</u>	<u>MIX #3</u>
BAMO-AMMO	17.5	23.45	17.5
GAP-P	13.125	5.687	13.125
BAMO	4.375	5.863	4.375
AP (200 micron)	45.5	45.5	0
AP (20 micron)	19.5	19.5	0
CL-20 (200 micron)	0	0	45.5
CL-20 (50 micron)	0	0	19.5

EXPERIMENTAL

General

Proton nuclear magnetic resonance spectra were recorded with a Varian XL-300 spectrometer operating at 300 MHz. Gel permeation chromatograms were obtained with a Waters chromatograph using four columns with exclusion sizes of 10^5 , 10^4 , 10^3 , and 10^2 Å. Tetrahydrofuran was used as the elution solvent. Refractive index was used for polymer detection. Hydroxyl equivalent weight was determined by a standard method using an automatic titrator. DSC results were obtained using a DuPont Model 910 DSC cell controlled by a Model 1090 thermal analyzer. Compressive mechanical properties were determined using an Instron Model 1125 universal testing machine at a crosshead speed of 20 in/min. A digital storage oscilloscope was used for data capture. Energetic oxetane monomers were prepared according to the established procedures.⁸ Reaction solvents were dried from appropriate agents and distilled under nitrogen immediately prior to use. Butanediol was distilled from sodium and stored in a septum-sealed vial prior to use. $\text{BF}_3\text{-OEt}_2$, 2,4-toluenediisocyanate (TDI) and diphenyltin dichloride (DTD) were purchased from Aldrich chemical and used as received. All reaction flasks and syringes were dried at least 12 hours in an oven and cooled in a desiccator over CaSO_4 or under a dry nitrogen or dry argon purge. All reactions were run under dry inert gas with reagents introduced by syringe or cannula to avoid introduction of moisture or air.

Polymerization of NMMO (difunctional for restart ABA)

To a stirred solution of 0.21 ml (2.4 mmoles) of butanediol in 172 ml of CH_2Cl_2 were added 0.295 ml (2.4 mmoles) of $\text{BF}_3\text{-OEt}_2$. After 15 minutes, 100 ml (816 mmoles) of NMMO were added over 5 minutes. After 23 hours, the reaction was quenched by addition of 50 ml of saturated aqueous sodium carbonate solution and 200 ml of CH_2Cl_2 . The phases were separated and the aqueous phase was washed with a further 50 ml of CH_2Cl_2 . The combined organic phase was dried (MgSO_4) and the volatiles were removed under reduced pressure to afford the product as a mobile liquid. The mobile liquid was stirred with 200 ml of hexanes followed by decanting the hexanes. The hydroxyl equivalent weight was 9434 g/eq suggesting a molecular weight of 18868 g/mole based on a functionality of 2.

Restart polymerization of BAMO using NMMO (difunctional) as initiator

To a stirred solution of 14.1 g (0.75 mmoles) of NMMO (prepared as described in the previous experiment and dried by lyophilization) in 25 ml of CHCl_3 were added 0.09 ml (0.75 mmoles) of $\text{BF}_3\text{-OEt}_2$. After 15 minutes, 6.25 ml (46 mmoles) of BAMO were added over 5 minutes. The reaction was then warmed to 45°C and allowed to proceed for 160 hours. The reaction was quenched by pouring into 150 ml of methanol. The product precipitated and was isolated by simple filtration.

Polymerization of AMMO (difunctional for ABA linking)

To a stirred solution of 0.205 ml (2.3 mmoles) of butanediol in 188 ml of CH_2Cl_2 were added 0.285 ml (2.3 mmoles) of $\text{BF}_3\text{-OEt}_2$. After 15 minutes, 116 ml (911 mmoles) of AMMO were added over 5 minutes. After 45 hours, the reaction was quenched by addition of 50 ml of saturated aqueous sodium carbonate solution and 200 ml of CH_2Cl_2 . The phases were separated and the aqueous phase was washed with a further 50 ml of CH_2Cl_2 . The combined organic phase was dried (MgSO_4) and the volatiles were removed under reduced pressure to afford the product as a mobile liquid. The mobile liquid was stirred with 300 ml of hexanes followed by decanting the hexanes. The molecular weight was 24250 g/mole by ^1H NMR analysis.

Polymerization of BAMO (monofunctional for ABA linking)

To a stirred solution of 0.73 ml (7.1 mmoles) of benzyl alcohol in 58 ml of CH_2Cl_2 were added 0.44 g (1.7 mmoles) of Et_3OPF_6 . Immediately, 40 ml (294 mmoles) of BAMO were added. After 2 hours, the reaction was quenched by addition of 25 ml of saturated aqueous sodium carbonate solution and 100 ml of CH_2Cl_2 . The phases were separated and the aqueous phase was washed with a further 25 ml of CH_2Cl_2 . The combined organic phase was dried (MgSO_4) and the volatiles were removed under reduced pressure to afford the product as a mobile liquid. The solid was stirred with 200 ml of hexanes followed by decantation of the hexanes. The molecular weight was 7457 g/mole by ^1H NMR analysis.

Linking of BAMO (monofunctional) to AMMO (difunctional) to form ABA

To a stirred solution of 19.1 g (2.56 mmoles) of BAMO (prepared as described in the preceding experiment and dried by lyophilization) in 75

ml of CHCl_3 were added 0.39 ml (2.69 mmoles) of TDI and 0.20 g (0.58 mmoles) of DTD. The reaction was then warmed to 45°C and allowed to proceed for 48 hours. At this point, to the reaction were added 31.0 g (1.28 mmoles) of AMMO (prepared as described in the preceding experiment and dried by lyophilization) in 50 ml CHCl_3 by cannula. After 120 hours, the reaction was quenched by pouring into 250 ml of methanol. The product precipitated and was isolated by simple filtration.

Polymerization of AMMO (difunctional for (AB)_n linking)

To a stirred solution of 5.79 ml (65.2 mmoles) of butanediol in 300 ml of CHCl_3 were added 360 ml (3.08 moles) of AMMO. The solution was warmed to 45°C and 1.2 ml (9.8 mmoles) of $\text{BF}_3\text{-OEt}_2$ were added. After 96 hours, the reaction was quenched by addition of 75 ml of saturated aqueous sodium carbonate solution and 300 ml of CH_2Cl_2 . The phases were separated and the aqueous phase was washed with a further 75 ml of CH_2Cl_2 . The combined organic phase was dried (MgSO_4) and the volatiles were removed under reduced pressure to afford the product as a mobile liquid. The mobile liquid was stirred with 300 ml of hexanes followed by decanting the hexanes. The hydroxyl equivalent weight was 2833 g/eq suggesting a molecular weight of 5666 based on a functionality of 2.

Polymerization of BAMO (difunctional for (AB)_n linking)

To a stirred solution of 2.95 ml (33.3 mmoles) of butanediol in 114 ml of CH_2Cl_2 were added 2.05 ml (16.7 mmoles) of $\text{BF}_3\text{-OEt}_2$. After 10 minutes, 80.8 ml (595 mmoles) of BAMO were added. After 16 hours, the reaction was quenched by addition of 50 ml of saturated aqueous sodium carbonate solution and 200 ml of CH_2Cl_2 . The phases were separated and the aqueous phase was washed with a further 50 ml of CH_2Cl_2 . The combined organic phase was dried (MgSO_4) and the volatiles were removed under reduced pressure to afford the product as a mobile liquid. The solid was stirred with 200 ml of hexanes followed by decanting the hexanes. The molecular weight was 3544 g/mole by ^1H NMR analysis.

Linking of BAMO (difunctional) to AMMO (difunctional) to form (AB)_n

To a stirred solution of 33.3 g (9.4 mmoles) of BAMO (prepared as described in the preceding experiment and dried by lyophilization) in 180 ml of CHCl_3 were added 2.71 ml (18.8 mmoles) of TDI and 0.15 g (0.44

mmoles) of DTD. In a second flask, to a stirred solution of 100.0 g (17.6 mmoles) of AMMO (prepared as described in the preceding experiment and dried by lyophilization) in 180 ml of CHCl_3 were added 5.08 ml (35.3 mmoles) of TDI and 0.15 g (0.44 mmoles) of DTD. Both reactions were then warmed to 45°C and allowed to proceed for 24 hours. At this point, the two reaction were combined and 2.40 ml (27.1 mmoles) of butanediol were added. After 48 hours more, the reaction was quenched by pouring into 250 ml of methanol. The product precipitated and was isolated by simple filtration.

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APPENDIX A

Application of ^1H NMR and FTIR to analysis of block-linking reactions.

Two analytical methods that complement and corroborate each other will in analyzing isocyanate-mediated block linking reactions of hydroxyl-terminated oxetane polymers are high field (300 MHz in this case) NMR and FTIR. The progress of the isocyanate plus alcohol to afford urethane product can be measured easily, giving a good indication of block linking. Being able to monitor the reaction precisely allows the tailoring of the reaction conditions to this system and more specifically for each polymer in a short time. The understanding of the unusual reactivity patterns of oxetane hydroxyl functionality with isocyanates that has been gained from this work also can have important implications for the use of similar materials in isocyanate-cured propellant systems.

An example of the application of these techniques is the synthesis of an $(\text{AB})_n$ block copolymer with BEMO hard block and BMMO/THF soft block. While these are not energetic blocks as used typically under this program, a complete set of the analytical data was obtained for this material and it serves as an example of the power of these analytical techniques. Figure A-1 shows the 300 MHz ^1H NMR spectra of the reaction of BEMO with TDI. The key resonances are labeled. The three small insets are from spectra acquired at increasing time of reaction with the lowest inset being the first acquired. The sample was obtained by removing a small aliquot from the reaction mixture, removing a large percentage of the solvent, dissolving in CDCl_3 , and treating with trifluoroacetic anhydride (TFAA). The TFAA reacts with alcohol endgroups that have not been converted to a urethane linkage. This allows easier identification and quantification of the endgroups which have and have not reacted. The insets show a progressively higher percentage of urethane endgroups compared to unreacted alcohol. Similarly, figure A-2 shows ^1H NMR spectra of the reaction of BMMO/THF with TDI. The method and conclusions from these spectra are identical to those for the BEMO reaction. Figure A-3 likewise reproduces the ^1H NMR spectra of the butanediol-linking reaction. As in the previous two spectra, the key resonances are labeled. The progress of the linking reaction is obvious from the relative intensities of the methylenes adjacent to the trifluoroacetylated alcohol and urethane linkages.

Parallel to the ^1H NMR spectra, FTIR spectra of the reactions were obtained to monitor the conversion of isocyanate functional groups to urethane functional groups. The spectra in figures A-4 and -5 were obtained by the reaction mixture with dichloromethane and directly acquiring a solution spectrum of the sample. These spectra obtained from samples of the same reaction of BEMO with TDI that was used for the NMR spectra presented in figure A-1. The isocyanate and urethane absorbencies are labeled. The conversion of isocyanate to urethane with increasing reaction time is apparent. Similarly, the spectra in figures A-6 and -7 were obtained from the reaction of BMMO/THF with TDI and parallel the NMR spectra in figure A-2. The higher isocyanate-to-urethane ratio in this material relative to that in the BEMO reaction reflects a deliberate stoichiometry difference to affect the product characteristics. Figures A-8 to -10 are FTIR spectra obtained on the butanediol linking reaction and parallel the NMR spectra in figure A-3. These spectra show the consumption of the isocyanate and conversion to urethane. These spectra do not show any evidence of other isocyanate coupling or degradation products. These methods together provide strong evidence for the formation of $(\text{AB})_n$ block polymers.

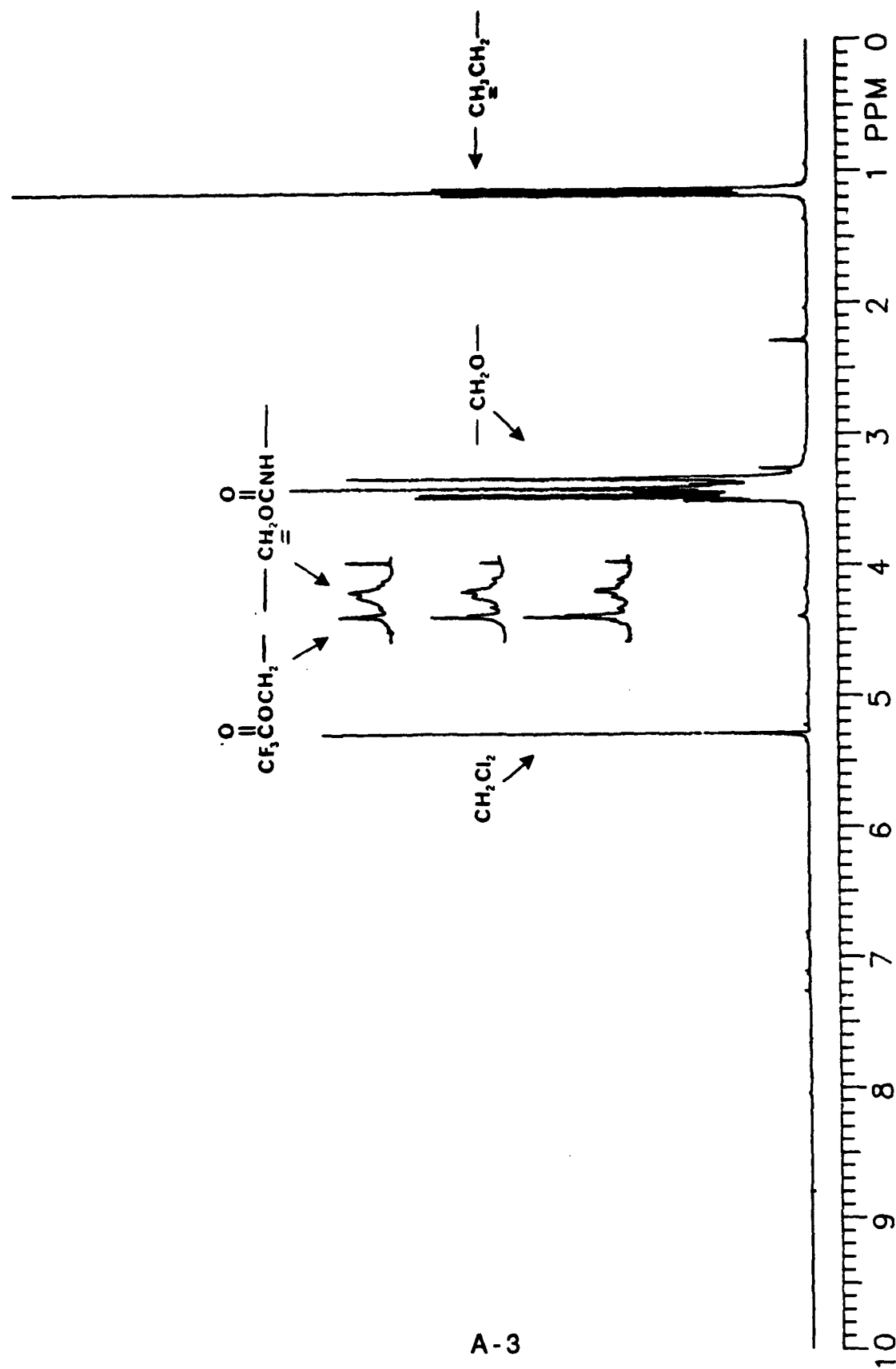


Figure A-1. 300 MHz ^1H NMR of the reaction of BEMO with TDI in CH_2Cl_2 with insets showing the progressive formation of urethane linkages.

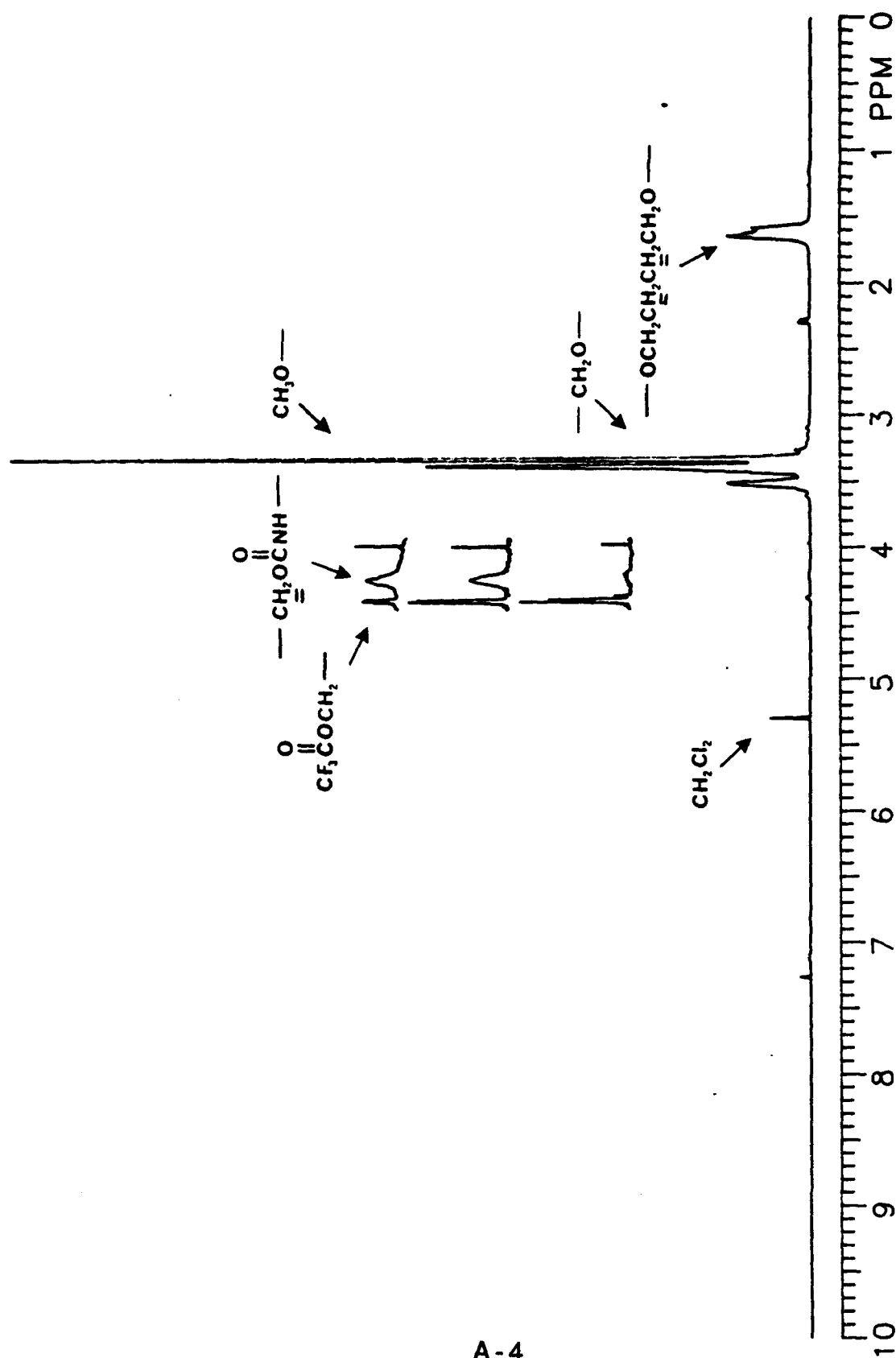
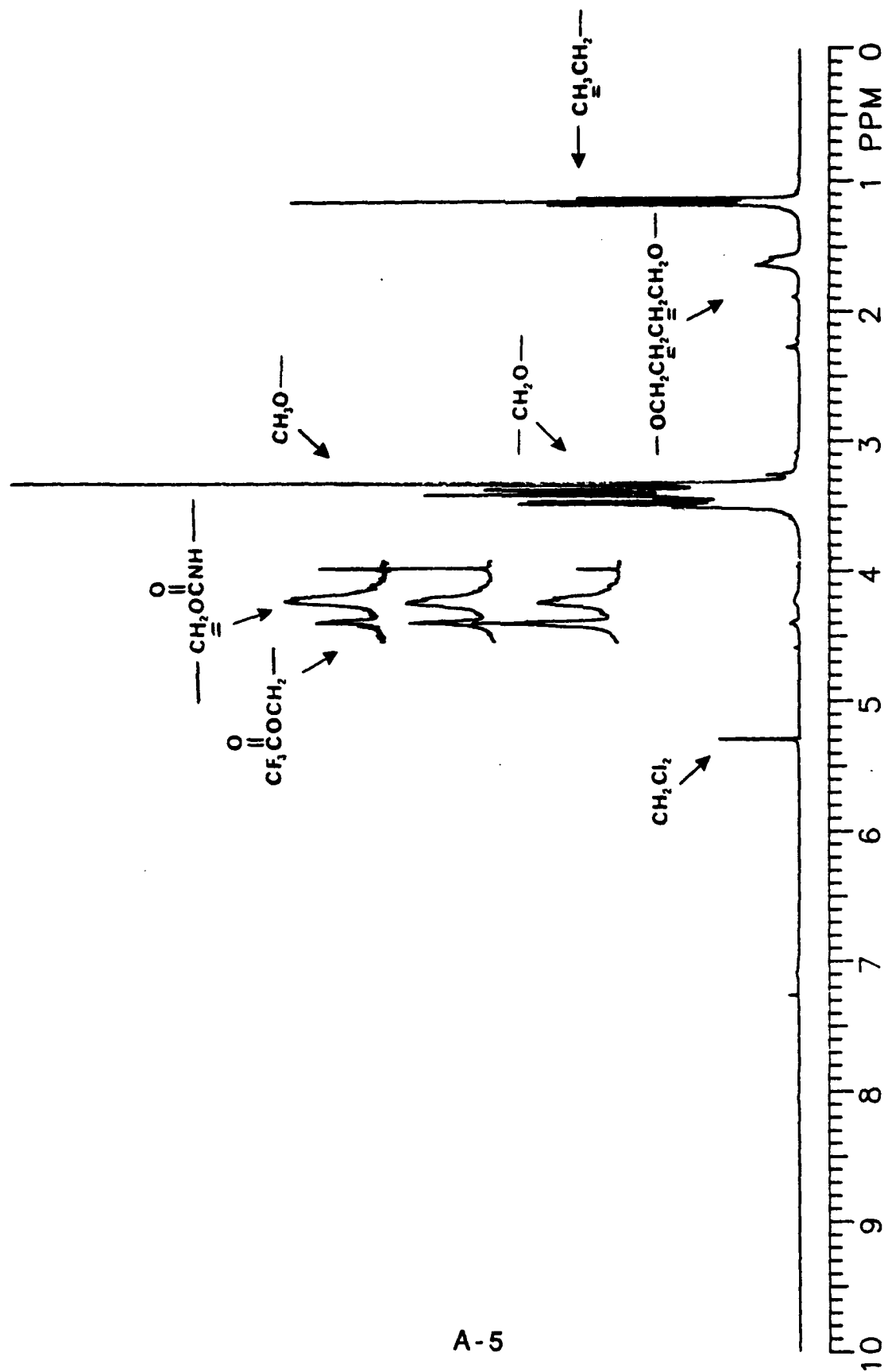


Figure A-2. 300 MHz ^1H NMR of the reaction of BMMO/THF with TDI in CH_2Cl_2 with insets showing the progressive formation of urethane linkages.



A-5

Figure A-3. 300 MHz ^1H NMR of the coupling of isocyanate-tipped BMO and BMMO/THF with butanediol in CH_2Cl_2 with insets showing the progressive formation of butanediol-derived urethane linkages.

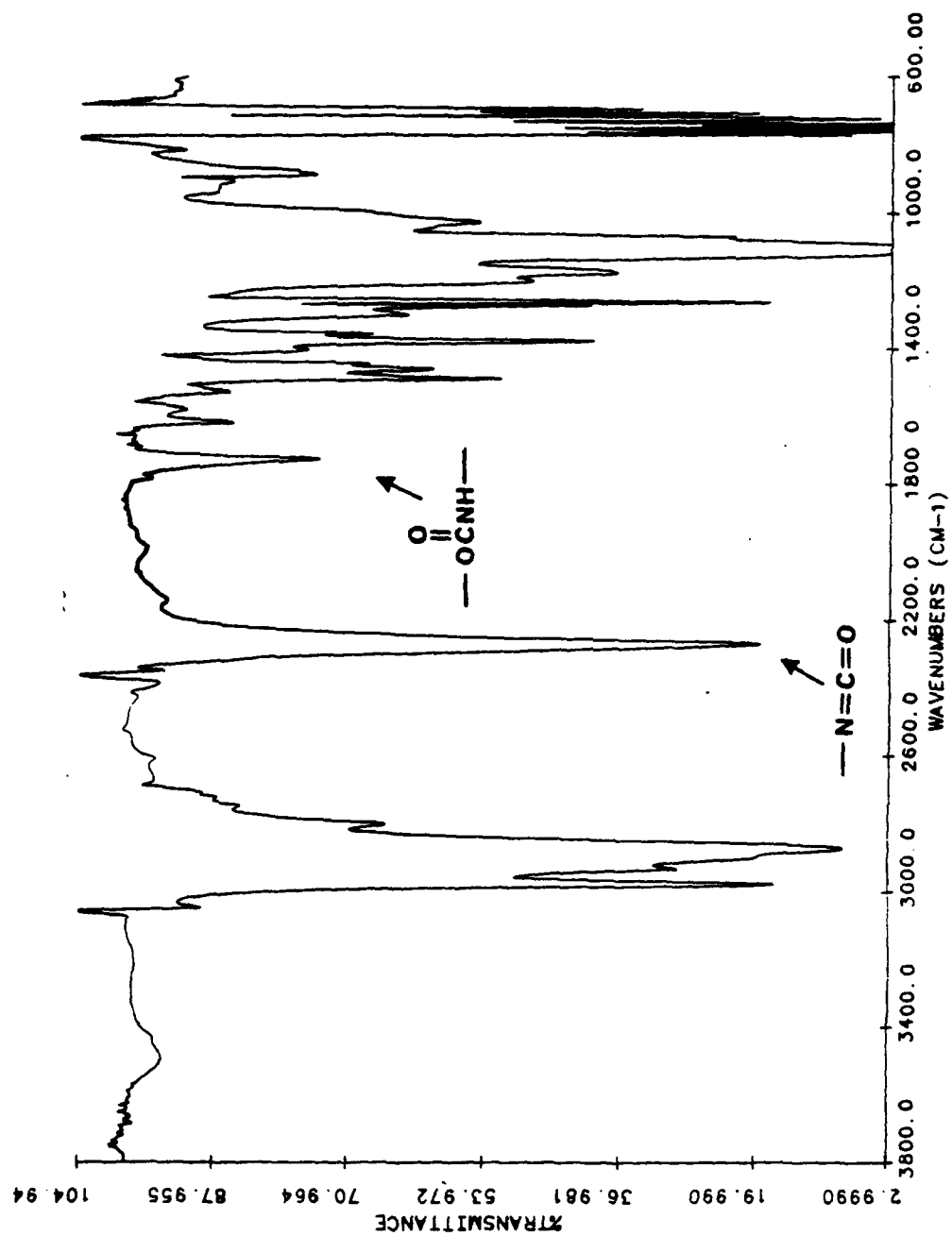
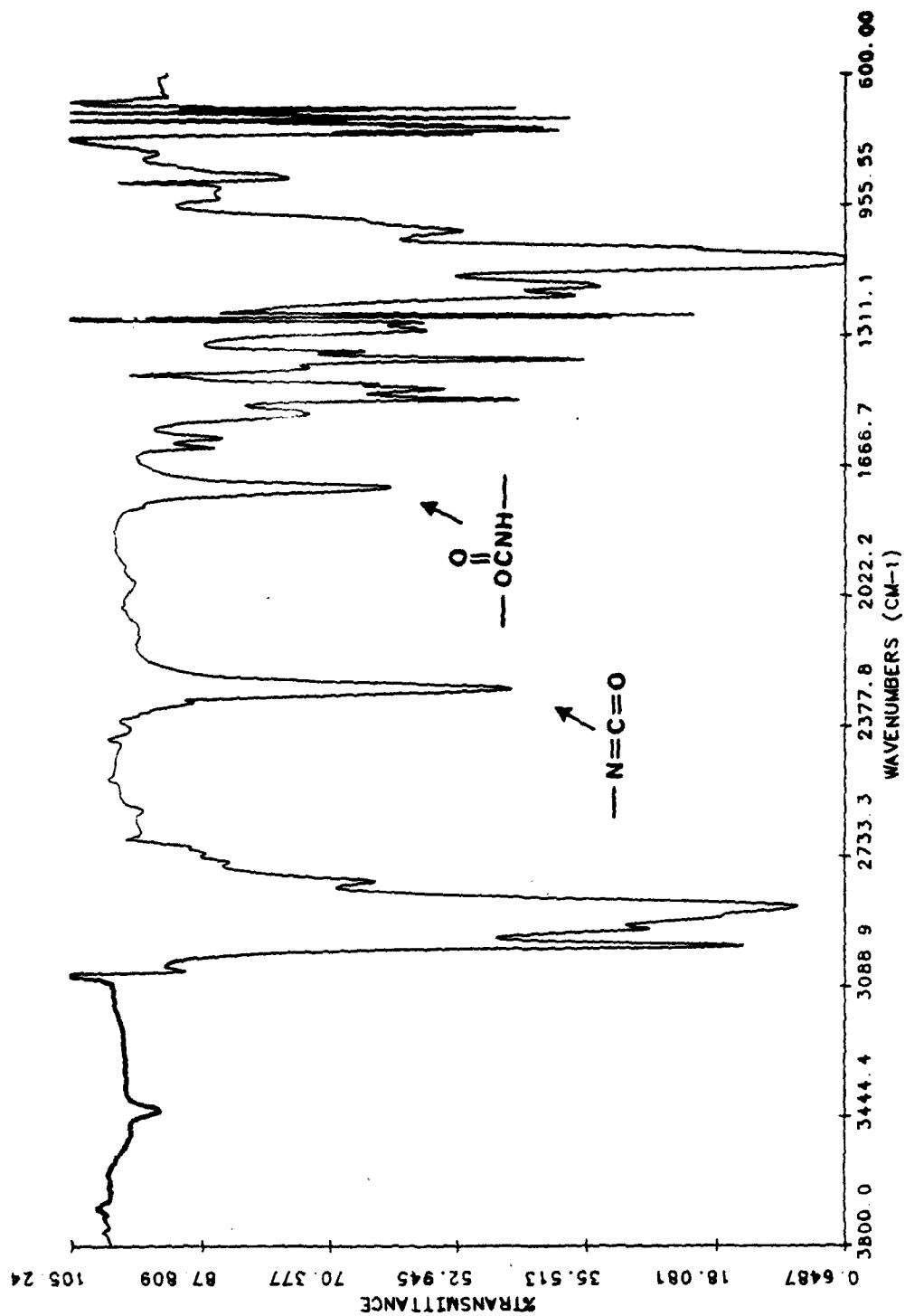
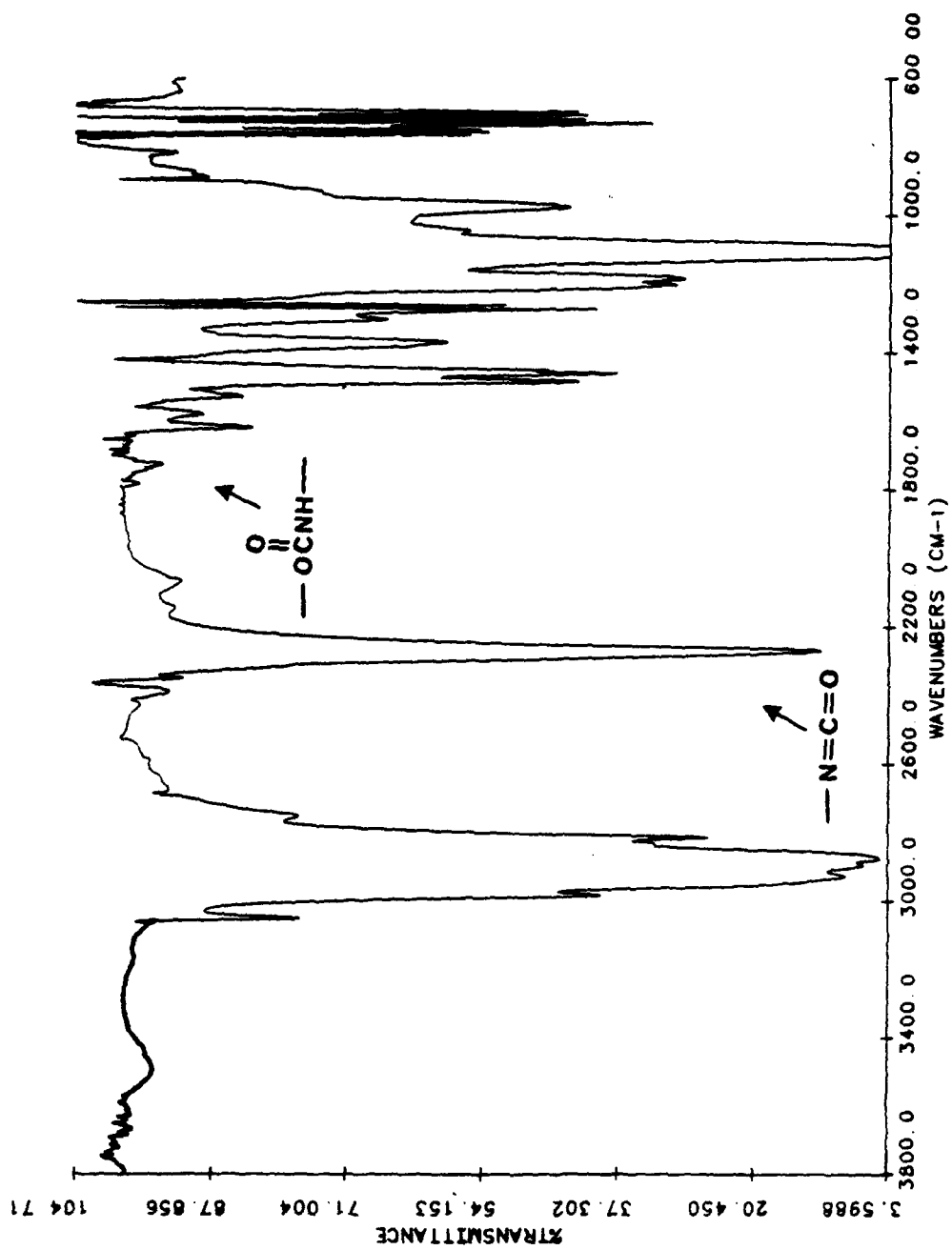


Figure A-4. FTIR spectrum 1.5 hours into the reaction of BEMO with TDI in CH_2Cl_2 showing isocyanate and urethane absorbencies.



A-7

Figure A-5. FTIR spectrum 47.5 hours into the reaction of BEMO with TDI in CH_2Cl_2 showing decreasing isocyanate and increasing urethane absorbencies.



A-8

Figure A-6. FTIR spectrum 1.75 hours into the reaction of BMMO/THF with TDI in CH₂Cl₂ showing isocyanate and urethane absorbencies.

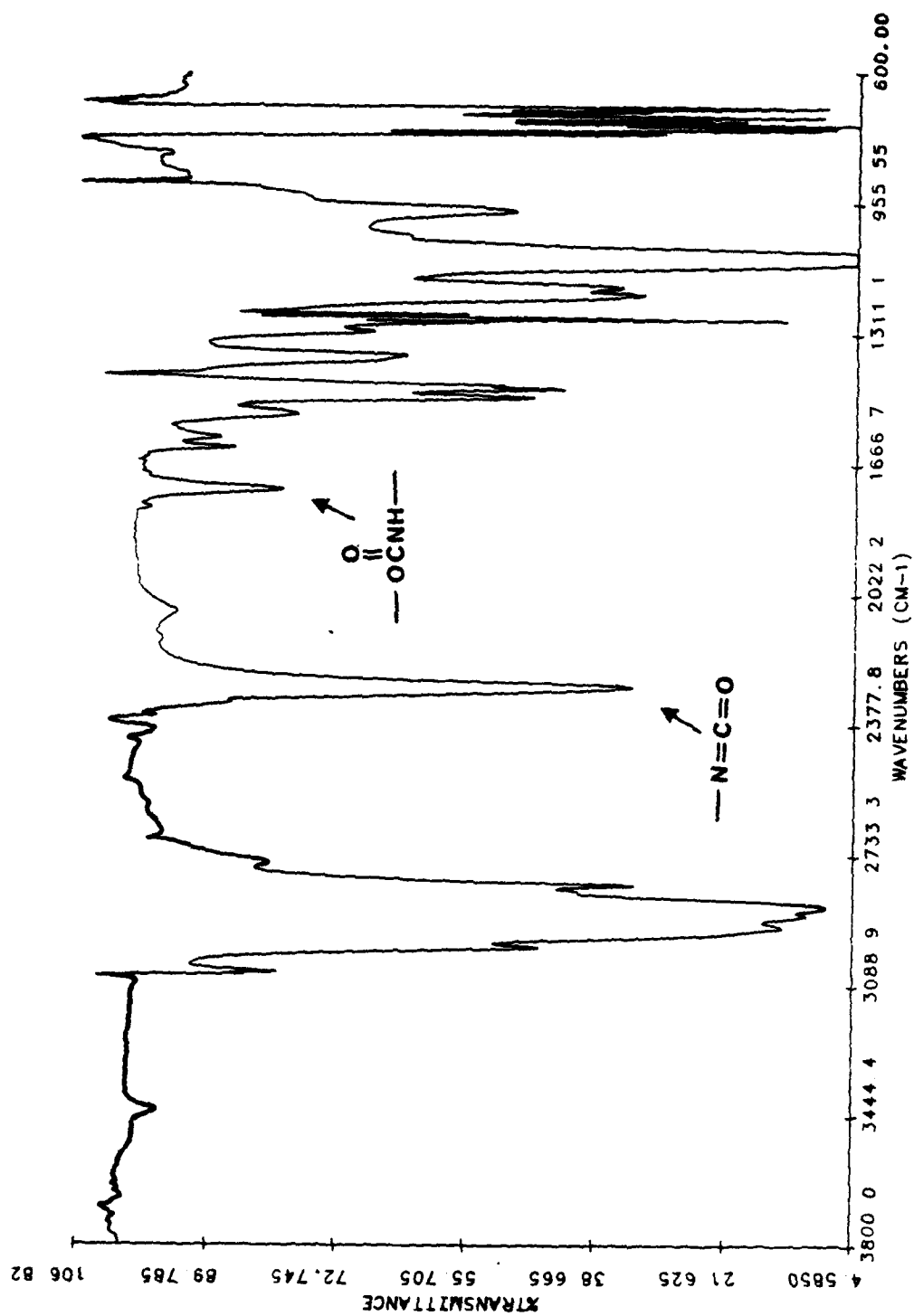


Figure A-7. FTIR spectrum 48 hours into the reaction of BMMO/THF with TDI in CH₂Cl₂ showing decreasing isocyanate and increasing urethane absorbencies.

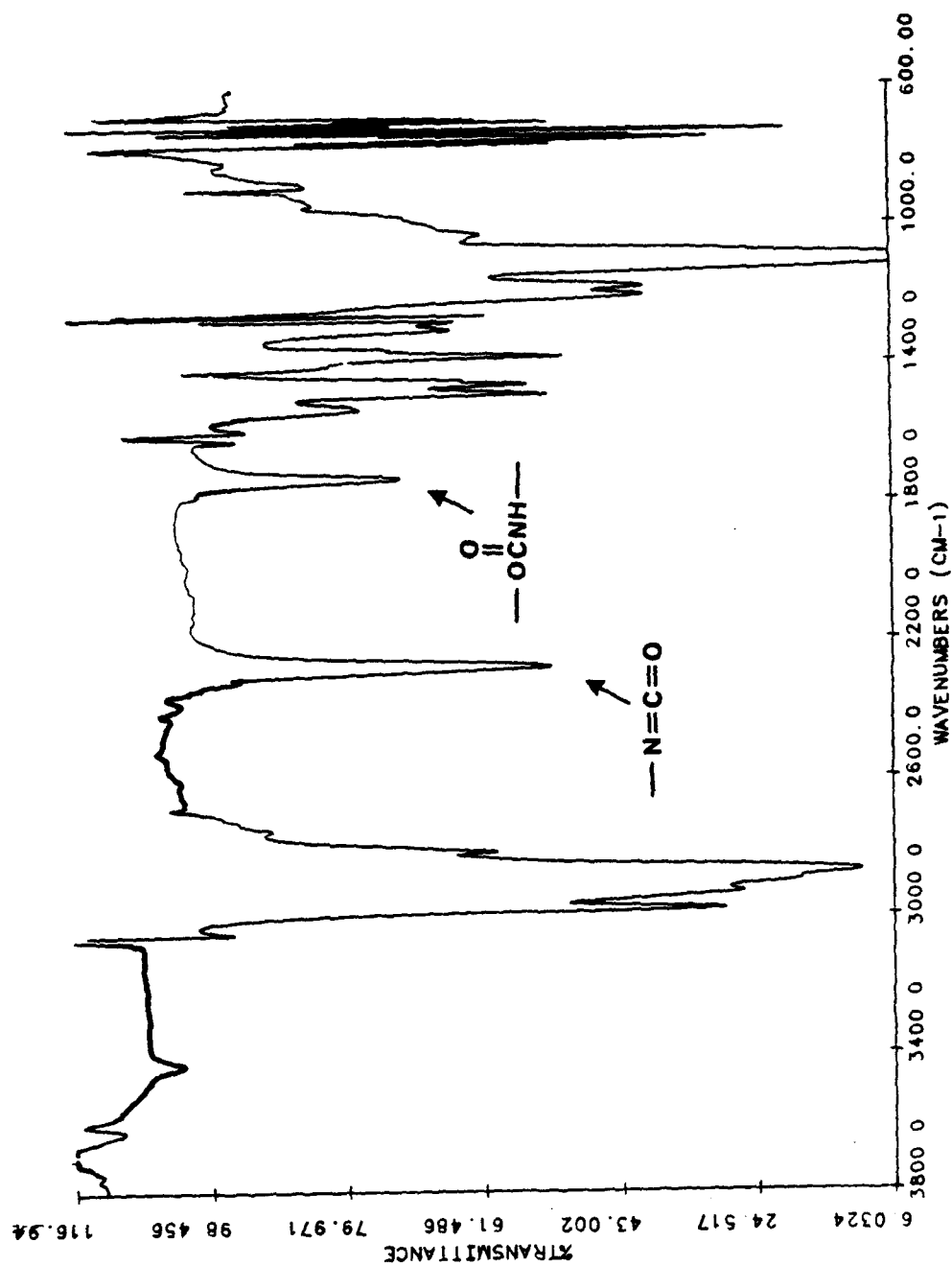


Figure A-8. FTIR spectrum 0.2 hours into the reaction of butanediol with the isocyanate-tipped BMO and BMMO/THF in CH_2Cl_2 showing isocyanate and urethane absorbencies.

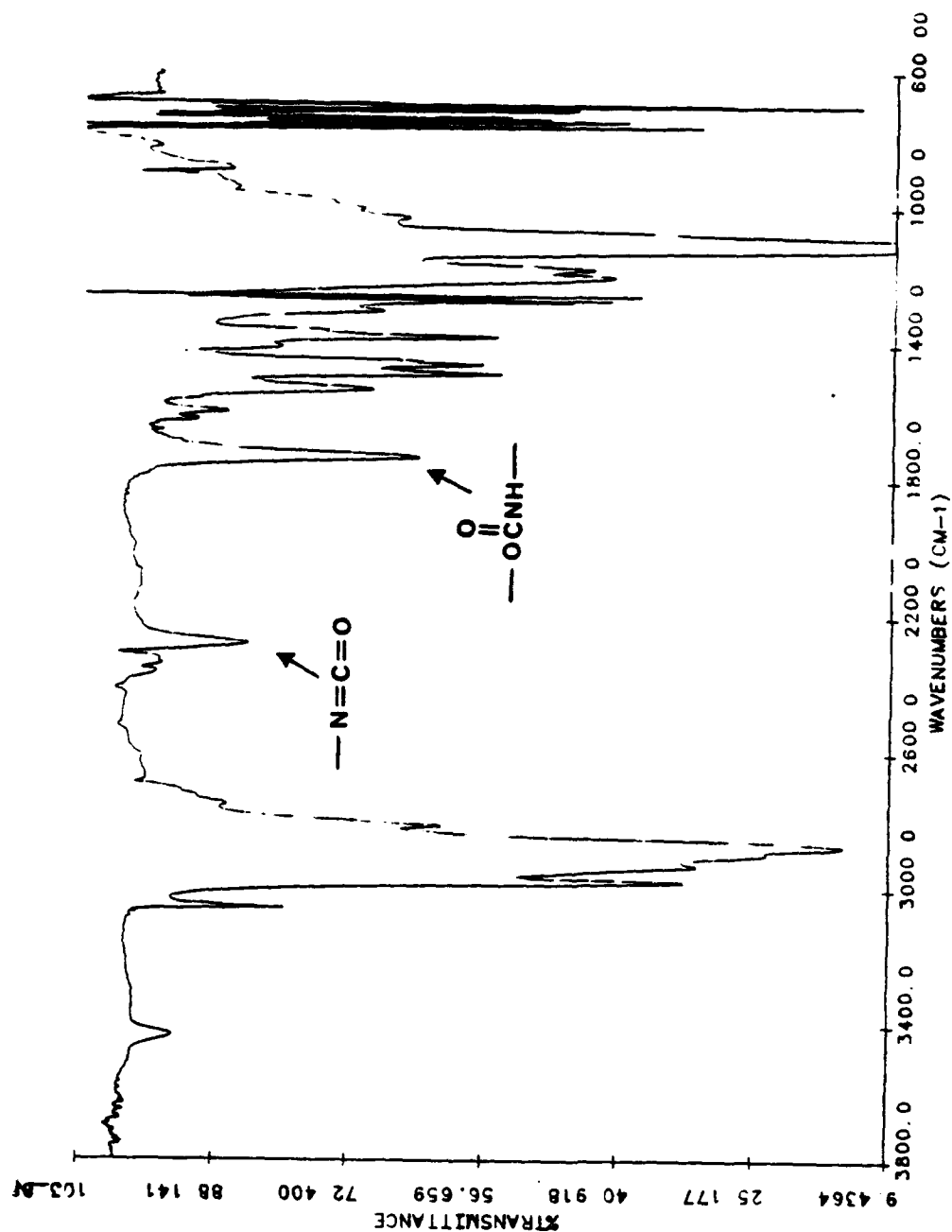


Figure A-9. FTIR spectrum 18 hours into the reaction of butanediol with the isocyanate-tipped BMO and BMMO/THF in CH_2Cl_2 showing decreasing isocyanate and increasing urethane absorbencies.

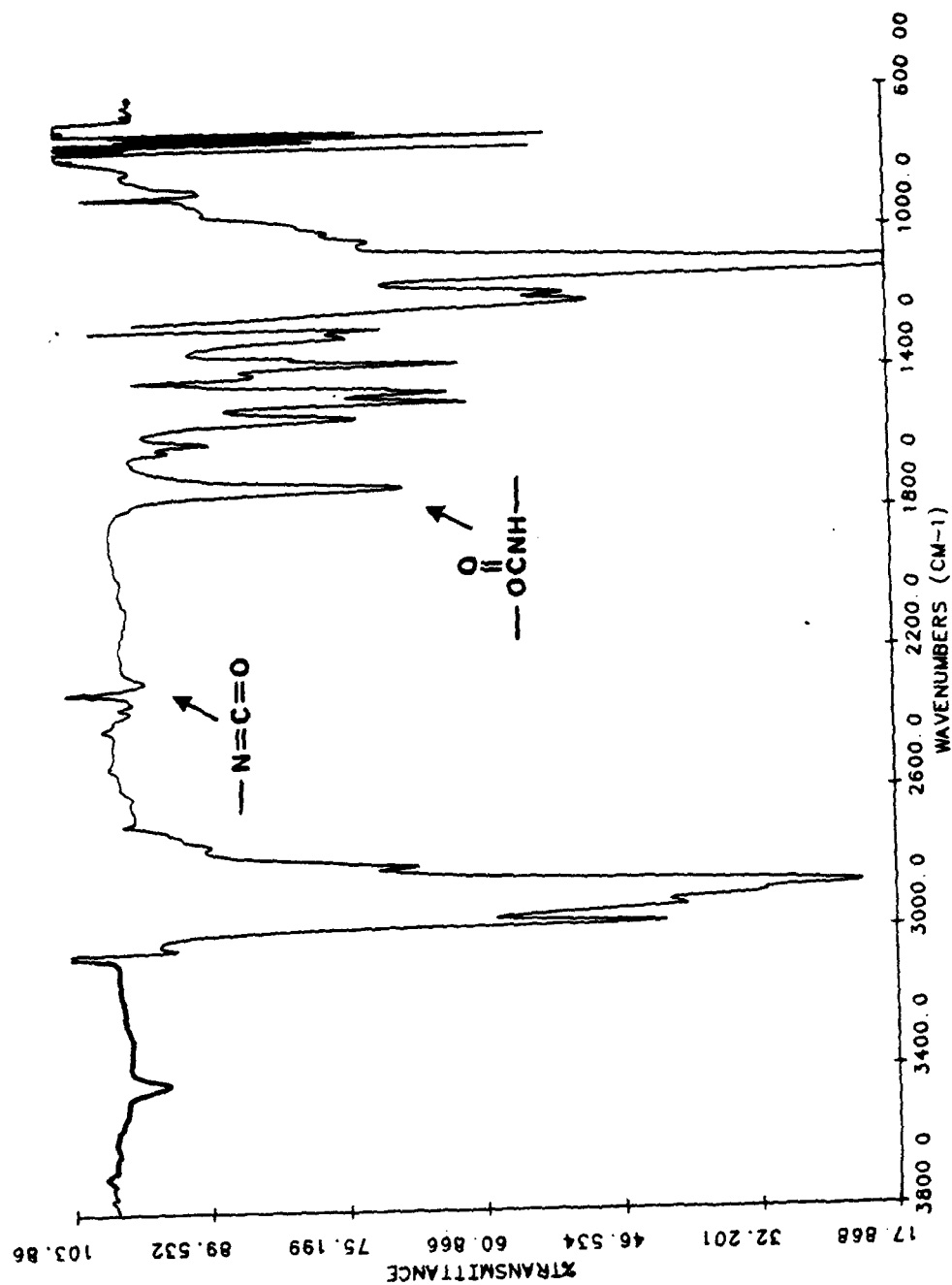


Figure A-10. FTIR spectrum 66 hours into the reaction of butanediol with the isocyanate-tipped BEMO and BMMO/THF in CH_2Cl_2 showing very small isocyanate and comparatively very large urethane absorbencies.

APPENDIX B

CHARACTERIZATION OF OXETANE POLYMERS BY HIGH FIELD NMR AND ASSOCIATED TECHNIQUES*

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ABSTRACT

The use of High Field NMR to elucidate the structure of polyoxetane materials will be discussed. NMR methods can be used to quantify initiator incorporation and position in the polymer (internal or terminal), to determine endgroup type and number, to measure randomness/blockiness of copolymers and to differentiate a mixture of homopolymers from block linked materials. Comparisons of these data with other experimental techniques to derive similar data and with mechanical properties will be made.

INTRODUCTION

During a recent investigation of the use of oxetane block copolymers with thermoplastic elastomer characteristics as LOVA binders,¹ a need arose for a rapid analytical technique for the determination of several key chemical parameters relating to polymer structure. A technique that appeared particularly well suited to the task was Nuclear Magnetic Resonance (NMR). NMR has been shown to be a powerful tool in the analysis of polymer structure.² NMR techniques have been reported in the literature to be used to determine hydroxyl equivalent weight in polyethylene glycol;³ to determine polymer microstructure in polyepichlorohydrin;⁴ and to prove the existence of a block copolymer in an ethylene-propylene sequential polymerization.⁵ A significant report⁶ was that of Groom and coworkers on the determination of hydroxyl endgroup number and chemical environment by derivatization in several polyether polyols with trifluoroacetic anhydride followed by ¹H or ¹⁹F NMR analysis. Several reports^{7,8,9,10,11} have been made on the use of NMR in the analysis of oxetane polymers. In this report, a description will be made of the experiments done to establish assignments for the several key NMR resonances and examples will be given of the application of NMR methods to answering structural questions of current interest in the oxetane field.

EXPERIMENTAL

All NMR spectra were obtained using a Varian XL-300 instrument operating either at 300 MHz for ¹H spectra or 75 MHz for ¹³C spectra. The two dimensional pulse sequences¹² are as provided in the Varian NMR software. HETCOR experiments were run under standard conditions assuming an average one bond ¹H-¹³C coupling of 140 hertz. The XCORFE spectra were obtained using multiple τ values to optimize the signal from two and three bond ¹H-¹³C couplings. The 3,3-bis(azidomethyl)oxetane (BAMO) low molecular weight polymer was prepared by the activated monomer method.¹³ The low molecular weight 3-azidomethyl-3-methyloxetane (AMMO) and the AMMO-BAMO copolymer, which was intended

*Approved for public release; distribution is unlimited.

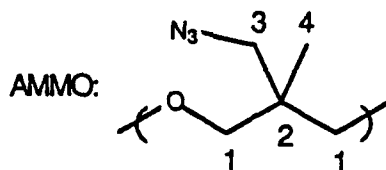
to be an ABA block copolymer, were obtained by a sequential polymerization.¹³ The AMMO monomer was initiated with butanediol and allowed to polymerize to completion. At that time, a small aliquot was removed, quenched and analyzed so that information on the intermediate AMMO could be obtained. A charge of BAMO monomer was then added and allowed to polymerize to near completion then quenched and the AMMO-BAMO copolymer isolated.

RESULTS AND DISCUSSION

A standard 300 MHz ^1H NMR of a low molecular weight difunctional BAMO polymer initiated with butanediol is given in Figure 1. The major resonances are easily assigned. The protons attached at C-1 and C-3 appear at $\delta 3.2$ - 3.5 while the signal at $\delta 1.6$ arises from the protons on C-2 and C-3 of butanediol (these carbons are equivalent if R and R' are the same). The signal at $\delta 3.6$ was tentatively assigned to the methylene adjacent to an alcohol end group. No signal relating to a butanediol derived alcohol endgroup was visible



in this spectrum. Treatment of the sample with trifluoroacetic anhydride served to verify the assignments made. As shown in Figure 2, the signal due to the methylene adjacent to the trifluoroacetyl moiety is at $\delta 4.29$ with no butanediol derived endgroup visible. The absorbance due to the butanediol is unaffected, adding strength to the argument that no butanediol endgroups exist in this material. Integration of the several absorbances allows measurement of hydroxyl equivalent weight, initiator incorporation, functionality and presence of minor impurities (note the weak CH_2Cl_2 signal at $\delta 5.28$). Comparison of these data to the target properties can provide insight, in a very simple and rapid experiment, into the efficiency of a given polymerization at attaining the desired product. Similarly, the 300 MHz ^1H NMR of a low molecular weight AMMO polymer which has been treated with trifluoroacetic anhydride shown in Figure 3 serves as an example of the peak assignments made for this material. The peak near $\delta 1.0$ is assigned to the protons attached to C-4 while the large peak near $\delta 3.2$ is assigned to the protons attached to C-1 and C-3. Obvious



in this spectrum are the two endgroup resonances at $\delta 4.22$ and $\delta 4.36$ which are assigned, respectively, to an AMMO derived endgroup and a butanediol derived endgroup. Confirming the butanediol endgroup is the existence of a signal at $\delta 1.82$ arising from the protons attached to C-3 of butanediol (R'=trifluoroacetate in butanediol structure). Shown in Figure 4 is the 300 MHz ^1H NMR spectrum of a trifluoroacetic anhydride treated AMMO-BAMO material which was prepared with a butanediol initiator with the two monomers polymerized sequentially in an attempt to form an ABA block copolymer. Assignments in

this spectrum are identical to those in the respective homopolymer. The resonances at $\delta 3.73$ and $\delta 4.61$ are due to unreacted BAMO monomer. From these data, conclusions can be drawn about the effectiveness of the polymerization reaction in preparing the desired ABA block copolymer with the desired molecular weight. The integration of the endgroup absorbences relative to the backbone and initiator absorbences, shows that good molecular weight control was achieved and that a high percentage of the butanediol initiator was incorporated into the polymer. However, the presence of three endgroup types in ratios of approximately 60:35:5 (BAMO:AMMO:butanediol derived) positively shows that the reaction was only partially successful in forming the desired ABA material. Based on these data, it is easy to conclude that this type of experiment is valid as a simple screening test for purported ABA materials. A true ABA material would have endgroups derived only from the 'outermost' block in the polymer. An NMR spectrum with exclusively the correct endgroups is a necessary condition for an ABA structure but is not sufficient to prove that structure.

Further information about the structure of oxetane polymers is obtained by ^{13}C NMR. Since discussions of the assignments of major peaks in ^{13}C NMR spectra of oxetane materials have been given elsewhere,^{10,11} a repetition of the listings would be redundant. However, several of the experiments done in the effort to fully assign both ^1H and ^{13}C NMR spectra by use of two dimensional techniques¹² shed further light on the structure of these materials. Two complimentary two dimensional pulse sequences were employed: HETCOR and XCORFE. The HETCOR pulse sequence, with the parameter set used, provides information on single bond ^1H - ^{13}C connectivities. The XCORFE sequence applied selects two and three bond ^1H - ^{13}C connectivities. As examples, spectra obtained from the three samples whose ^1H NMR spectra were described above will be presented.

In Figures 5 and 6 respectively are shown the HETCOR and XCORFE spectra for the low molecular weight BAMO polymer. Assignment of the major peaks is obvious. Also clear using these sequences, particularly the XCORFE experiment, is the assignment of the ^{13}C signals that are slightly upfield from each of the major backbone resonances as arising from the BAMO residue adjacent to the trifluoroacetate derivative of the alcohol endgroup. In the spectra of the AMMO polymer shown in Figures 7 and 8, similar information is again apparent. In these spectra, the signal ^{13}C signals related to the butanediol initiator derived endgroups can be assigned. The two small peaks just upfield from the major butanediol ^{13}C resonances arise from a butanediol endgroup as does the ^{13}C resonance at $\delta 68$. The HETCOR and XCORFE spectra of the sequentially polymerized AMMO-BAMO material are shown in Figure 9 and 10 respectively. Assignments as made from the other HETCOR and XCORFE experiments apply here. The signal relating to the linkage of the AMMO and BAMO blocks in the XCORFE spectrum was not strong enough to be unambiguously identified. This linkage has been observed in a more random AMMO-BAMO material and the fact that it is difficult to observe would be predicted for a block material with only a small number of covalently linkages between AMMO and BAMO residues. However, in the standard ^{13}C spectrum this linkage is easily identified. Shown in Figure 11 is an expansion of the quaternary carbon region of the fully relaxed ^{13}C spectrum of the AMMO-BAMO polymer. Assignment of the peaks appearing in this region has been made.¹¹ Most interesting is that while there are resonances for the all AMMO (A-A-A) triad, the all BAMO triad (B-B-B), and the triads predicted for the block linkage (A-A-B and B-B-A), none exist for the mixed copolymer triads (A-B-A and B-A-B). Further, the amount of

block linkage triad (A-A-B and B-B-A) relative to block triad (B-B-B and A-A-A) is near that predicted for the molecular weight targeted.

The combined ^1H and ^{13}C NMR data taken together suggest that a considerable amount of the desired block material has been prepared with the target molecular being achieved but that there is also considerable diblock material present. Comparison of the NMR data with GPC and hydroxyl equivalent data in Table I, show the good correlation of these experimental techniques. Of particular note are the polydispersities for the AMMO and the AMMO-BAMO materials. Had the material not formed a block material in which the blocks are covalently connected, the polydispersity would be expected to rise with an increase in molecular weight. This result corroborates the ^{13}C experimental data. It is interesting that of the data presented here (^1H and ^{13}C NMR, GPC and hydroxyl equivalent weight) only the ^1H NMR endgroup analysis gives any real indication of the deviation in structure from the desired ABA in the sequentially polymerized material. These results lead to the conclusion that the ^1H NMR endgroup analysis experiment is vital to the proper identification of structure in any oxetane material thought to be a block copolymer. The remarkable simplicity of this experiment make it the obvious first choice in the analysis of any oxetane material.

TABLE I.
Properties of Low Molecular Weight Oxetane Polymers^a

Material	Target	Hydr	GPC		NMR	
	MW	Eq Wt	Mw	Mn	Disp	MW
BAMO	1680	694	1600	1090	1.47	1363
AMMO	1270	682	1820	1300	1.44	1360
BAMO-AMMO	2920	1299	2910	2010	1.45	2390

^aThe data in this table show the good correlation between NMR titration and GPC determined molecular weight. That the AMMO-BAMO has the same polydispersity as the AMMO also supports the ^{13}C NMR data that the material is in fact a block copolymer.

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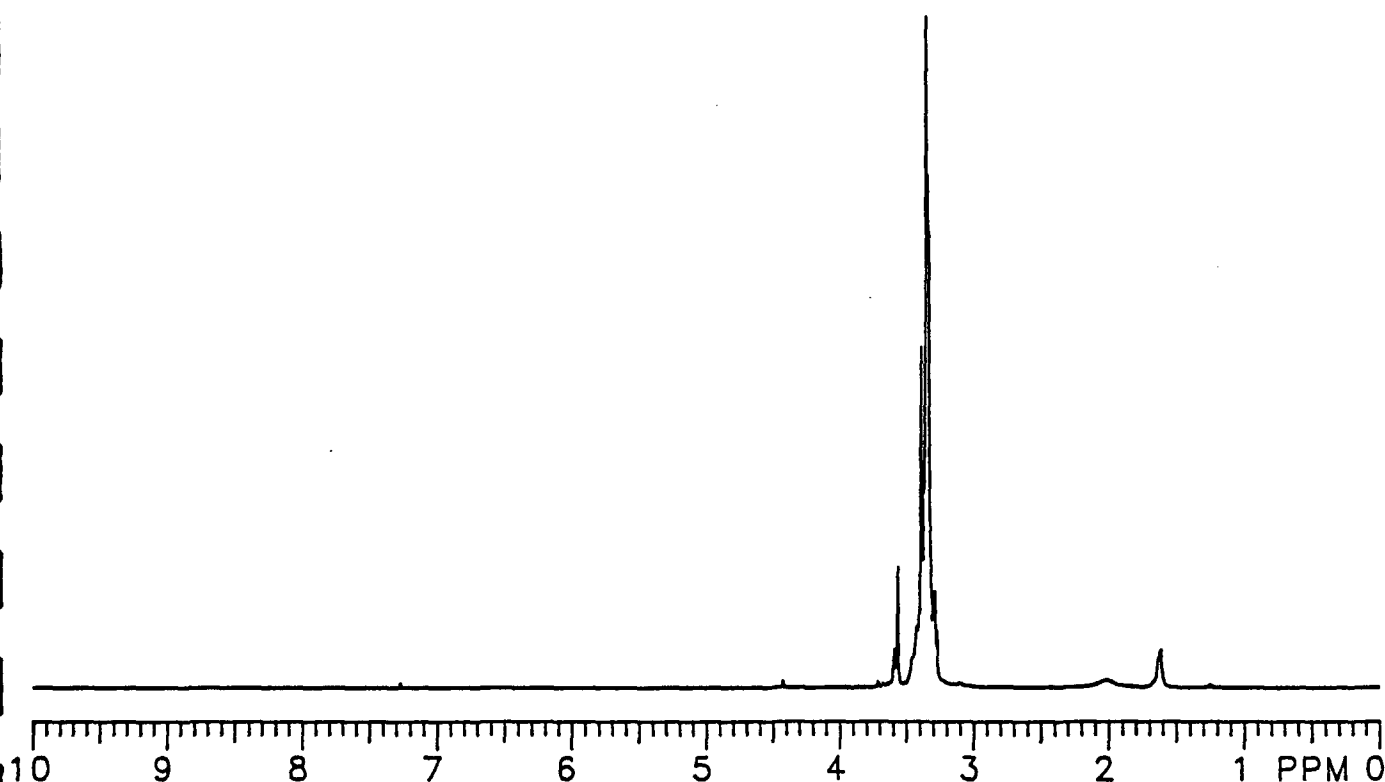


Figure 1. Shown here is the ^1H NMR spectrum of a low molecular weight BAMO.

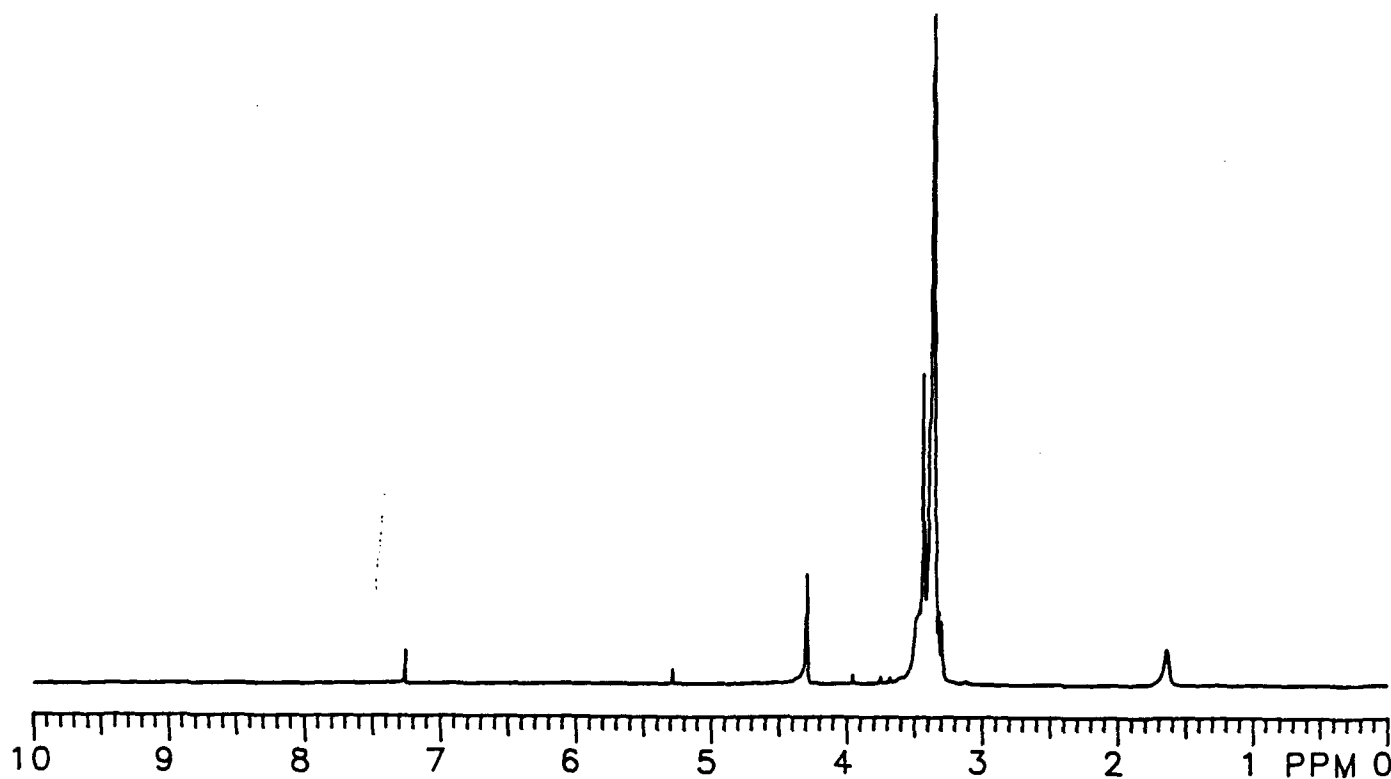


Figure 2. Shown here is the ¹H NMR spectrum of a low molecular weight BAMO that has been treated with trifluoroacetic anhydride. This results in the shifting of the resonance relating to the methylene adjacent to an alcohol functionality due to derivatization as the trifluoroacetate.

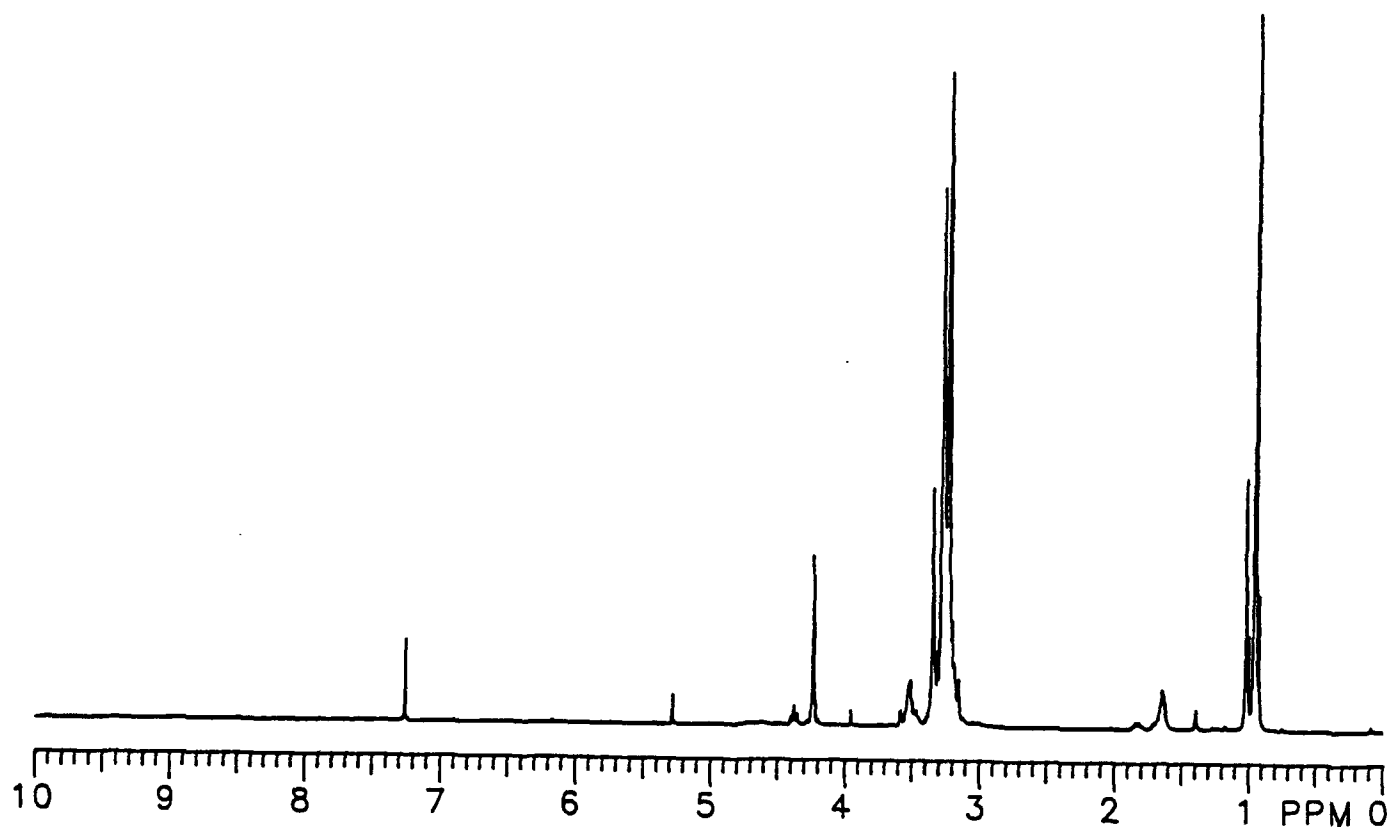


Figure 3. Shown here is the ¹H NMR spectrum of a low molecular weight AMMO that has been treated with trifluoroacetic anhydride. Alcohol endgroups as the trifluoroacetate derivative are clearly visible.

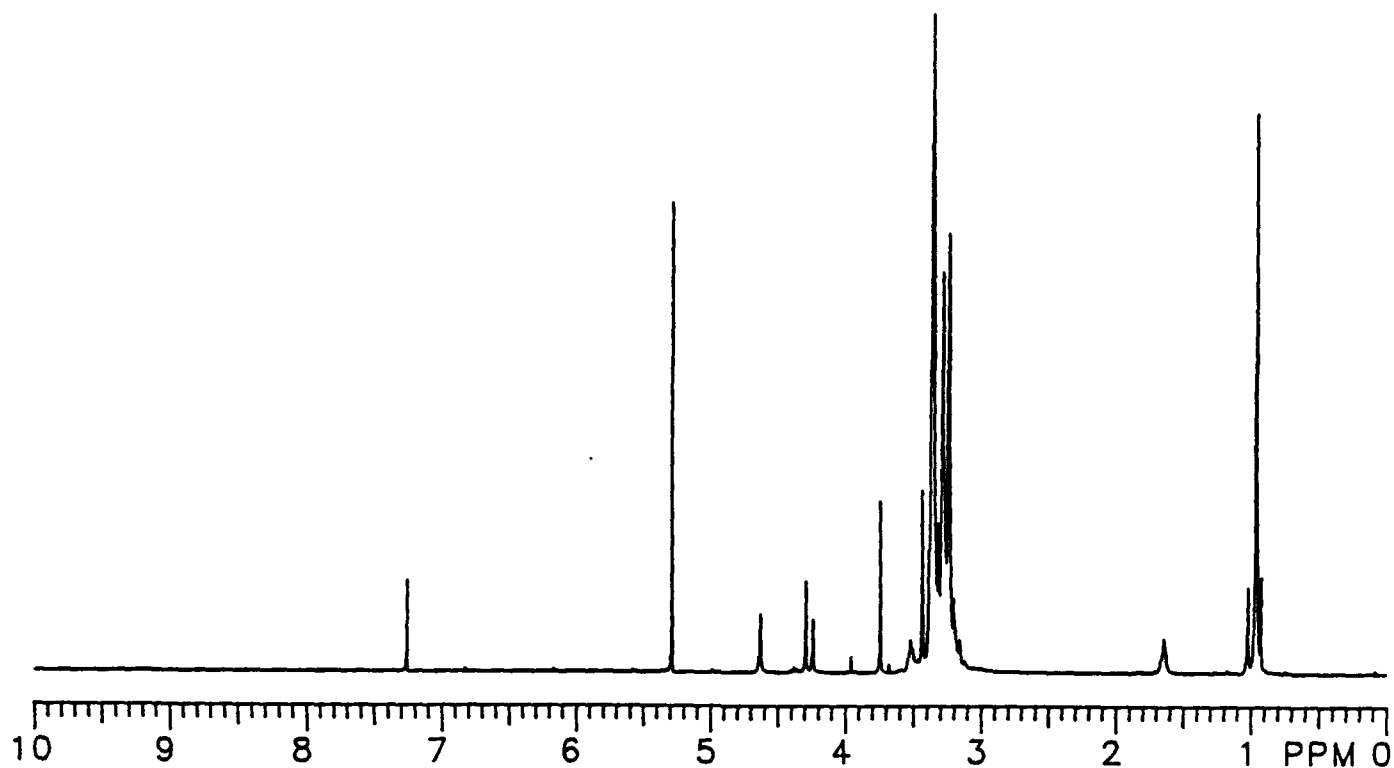


Figure 4. Shown here is the ^1H NMR spectrum of a low molecular weight AMMO-BAMO prepared by a sequential polymerization with an intended ABA block copolymer structure. The material has been treated with trifluoroacetic anhydride. Obvious in the spectrum is the presence of BAMO, AMMO and butanediol derived endgroups, showing clearly that the material is not exclusively the desired ABA structure.

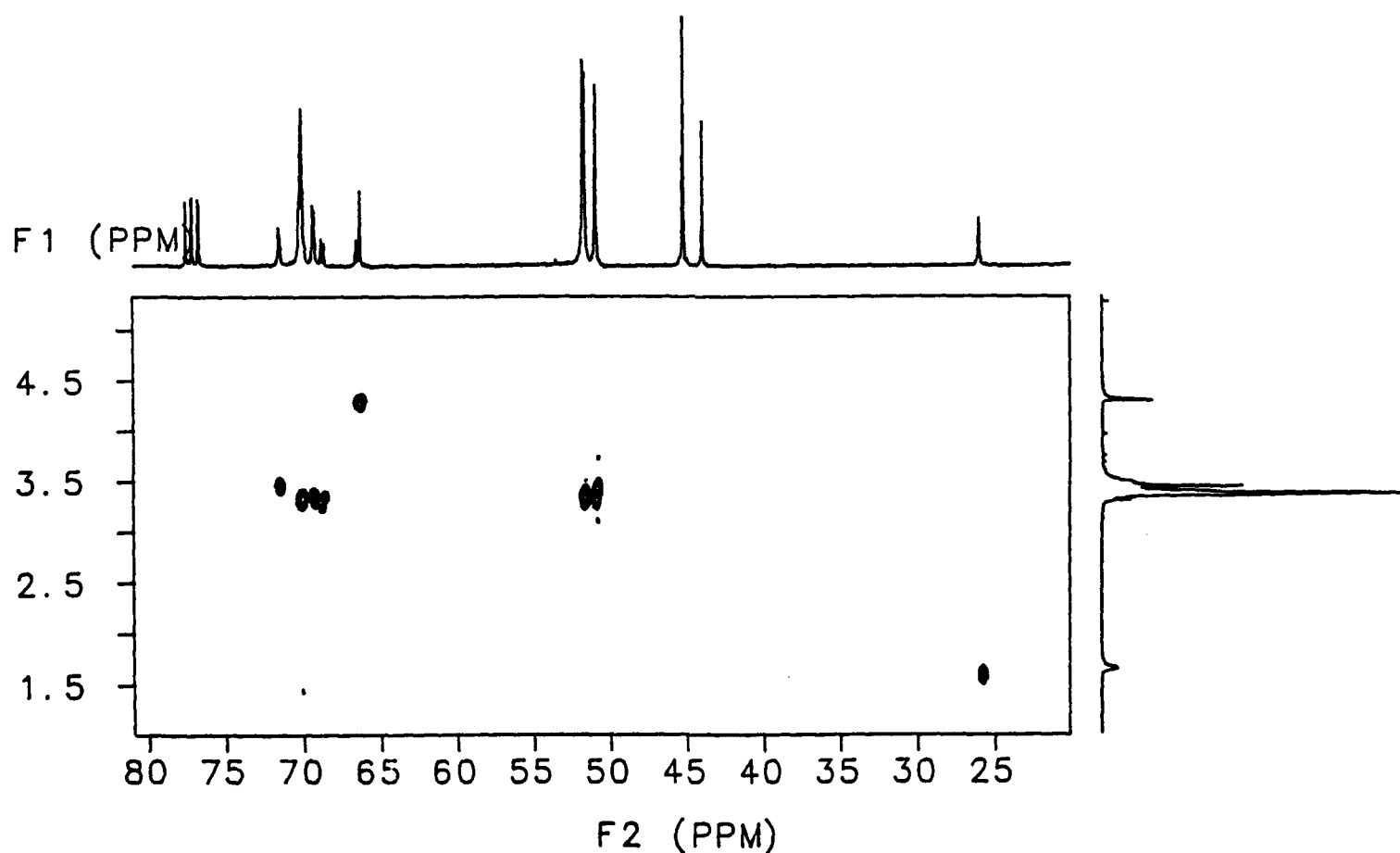


Figure 5. Shown here is the HETCOR spectrum of a low molecular weight BAMO. Clearly visible

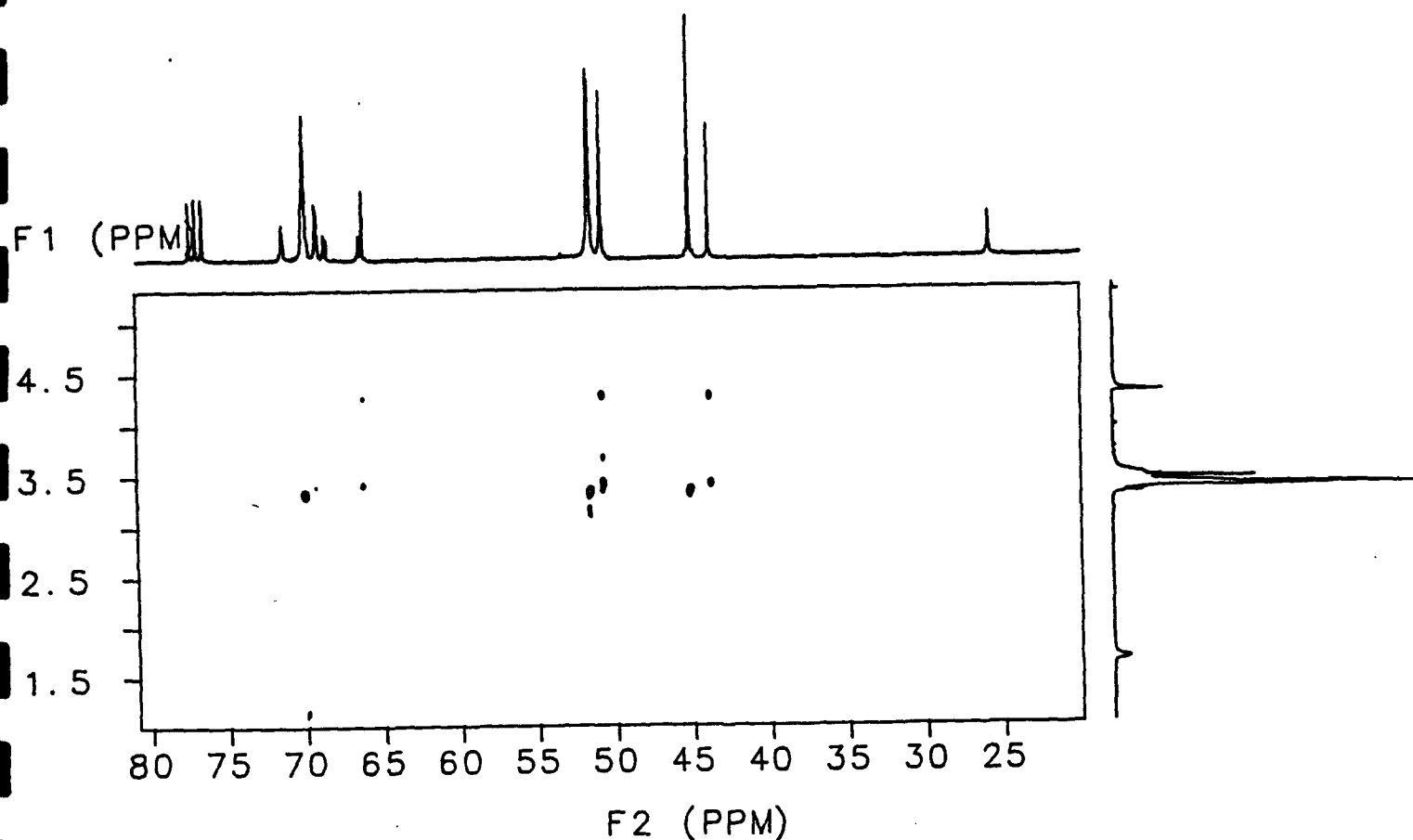


Figure 6. Shown here is the XCORFE spectrum of a low molecular weight BAMO. From these data, the assignment of several of the minor ^{13}C resonances can be made.

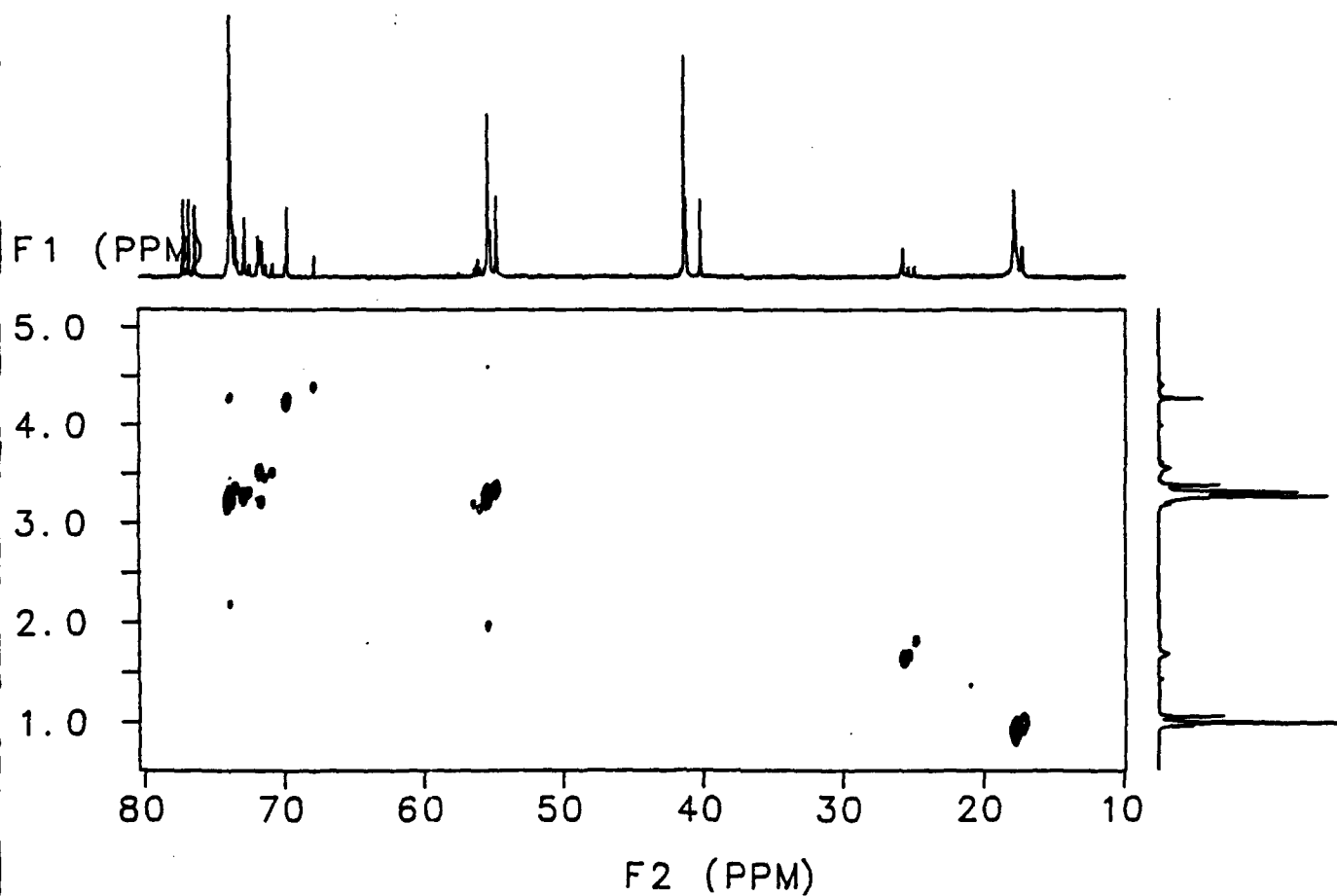


Figure 7. Shown here is the HETCOR spectrum of a low molecular weight AMMO. Clearly visible are the major $^{1\text{H}}\text{-}^{13}\text{C}$ correlations including endgroups.

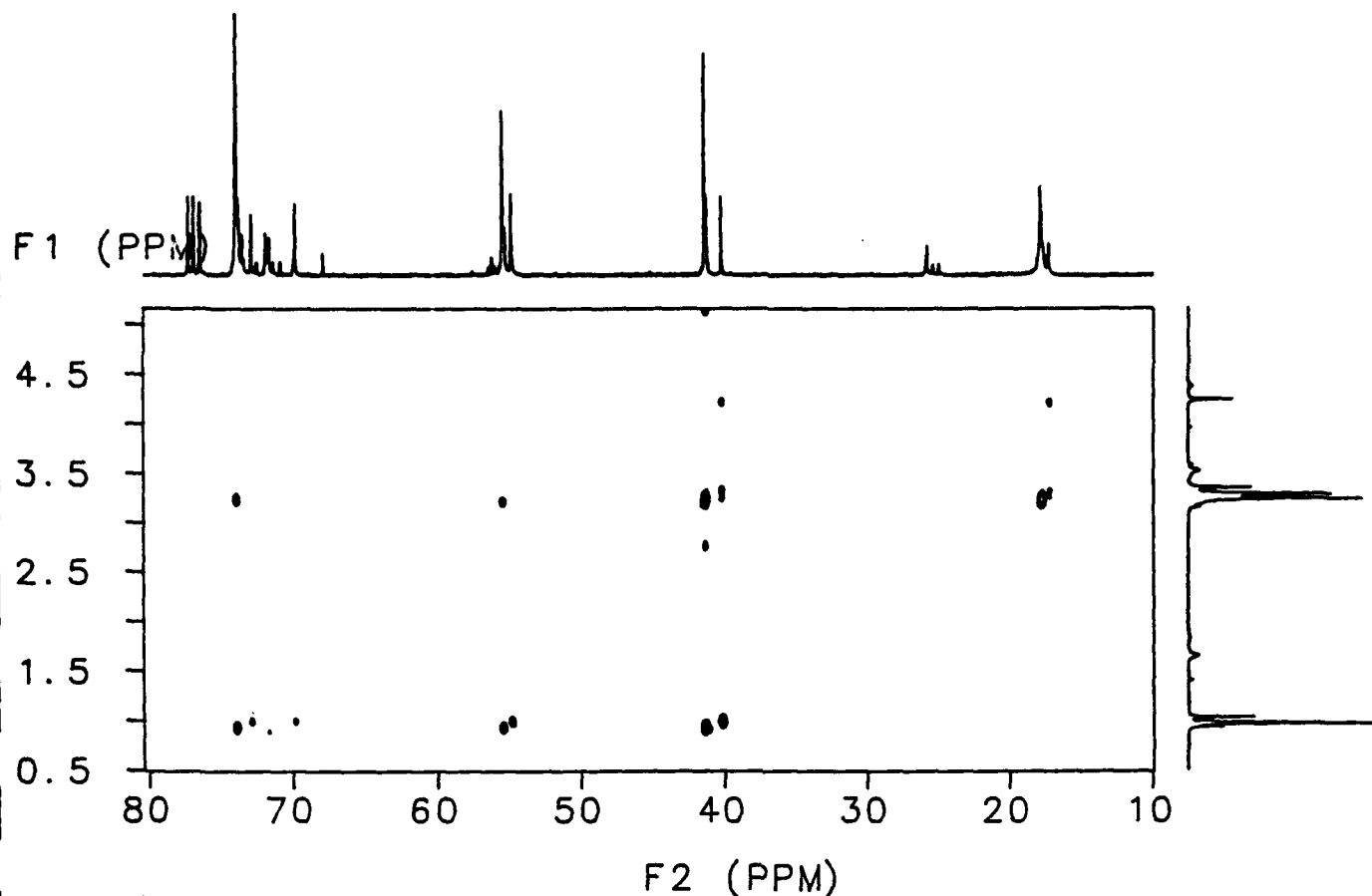


Figure 8. Shown here is the XCORFE spectrum of a low molecular weight AMMO. From these data, the assignment of several of the minor ^{13}C resonances can be made.

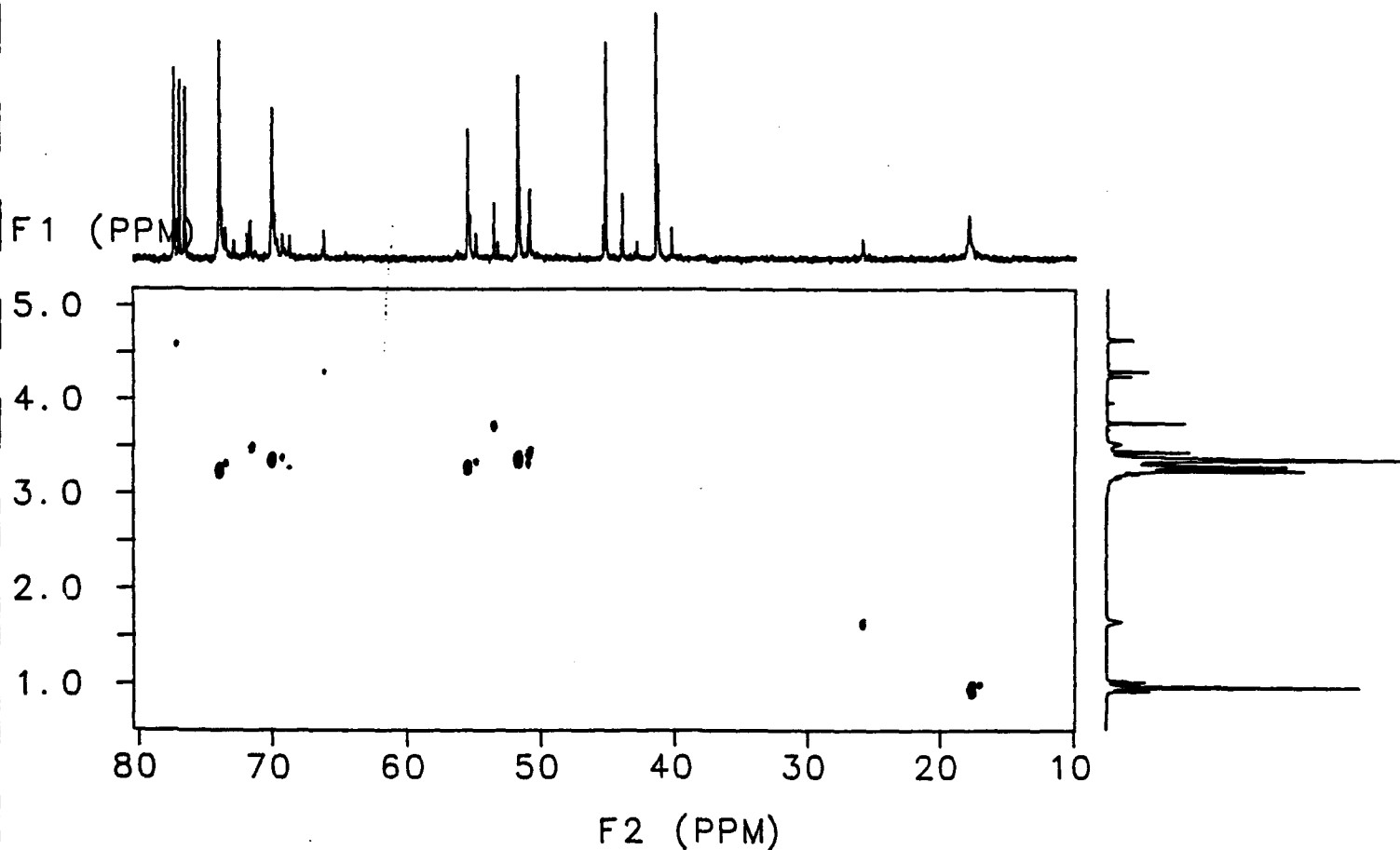


Figure 9. Shown here is the HETCOR spectrum of a low molecular weight AMMO-BAMO. Clearly visible are the major ^{13}C correlations.

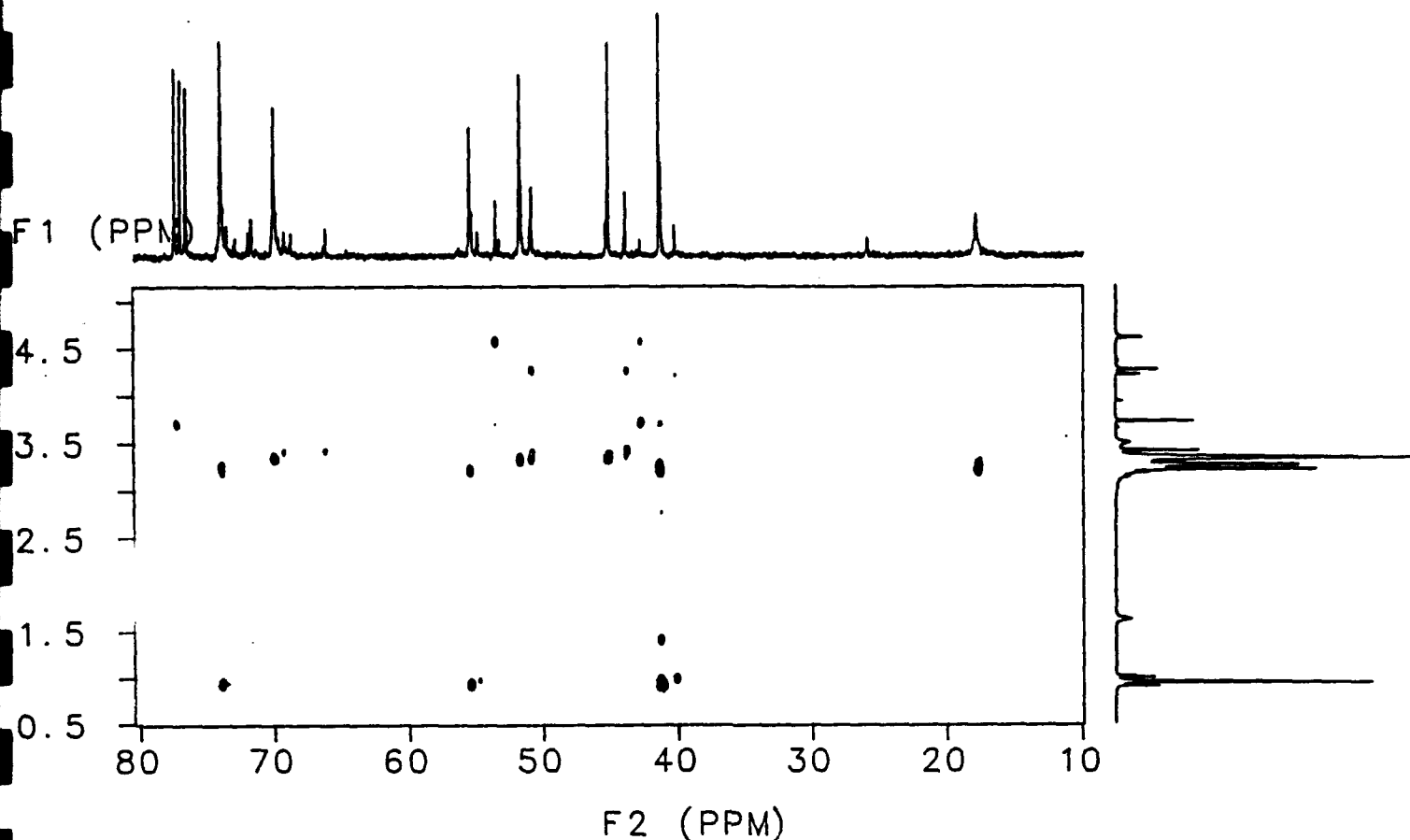


Figure 10. Shown here is the XCORFE spectrum of a low molecular weight AMMO. From these data, the assignment of several of the minor ^{13}C resonances can be made. Absent is any clear signal from an AMMO-BAMO linkage, suggesting that the material is not a random copolymer.

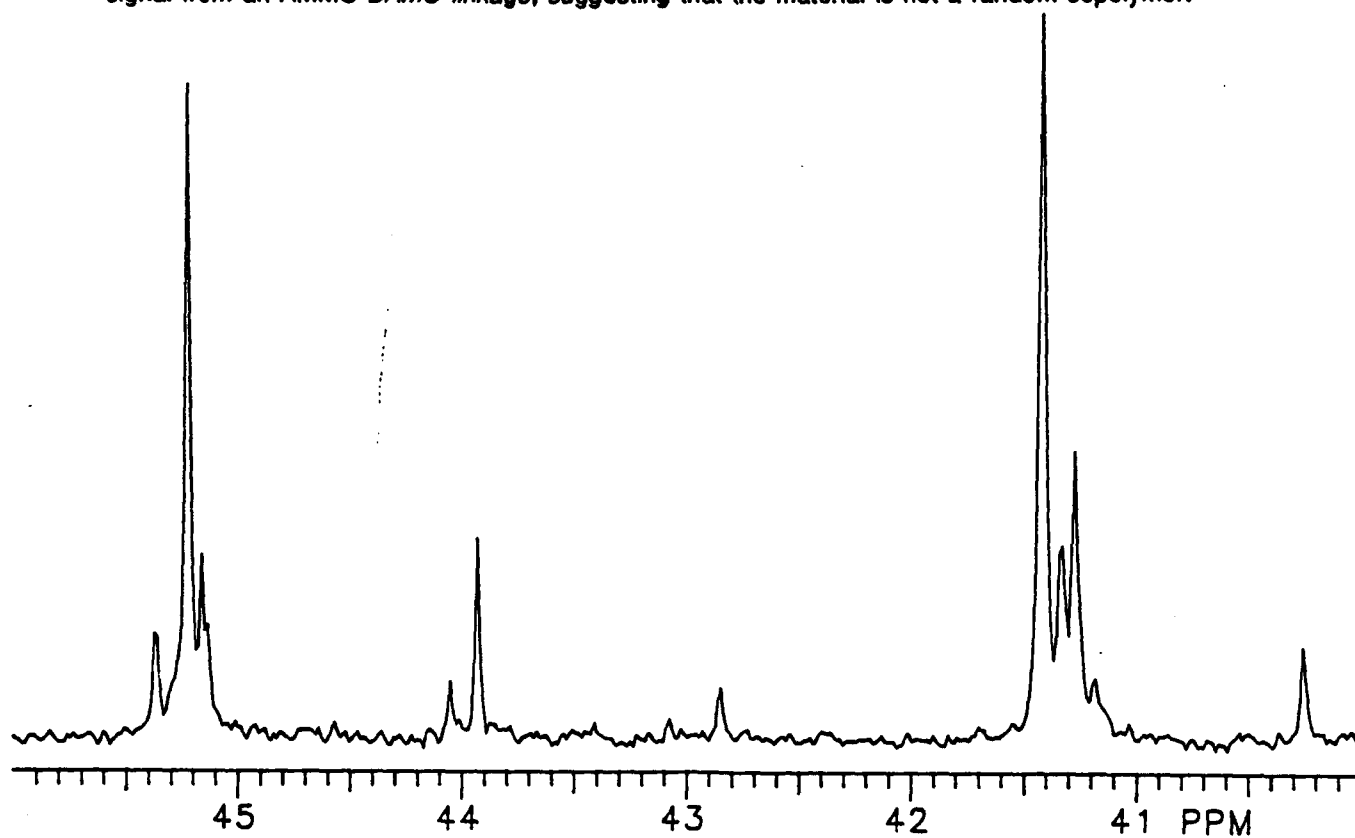


Figure 11. Shown here is an expansion of the quaternary carbon region of a ^{13}C spectrum of the low molecular weight AMMO-BAMO block copolymer. Clearly visible are the all AMMO and all BAMO triads (A-A-A: 841.42 and B-B-B: 845.19) and the triads predicted for the linkage (A-A-B: 841.34 and B-B-A: 845.44). No signals can be found for the mixed copolymer triads (B-A-B and A-B-A). The peak at 841.34 arises from the AMMO-BAMO linkage.

APPENDIX C

SYNTHESIS OF OXETANE ABA THERMOPLASTIC ELASTOMERS BY A BLOCK-LINKING APPROACH*

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ABSTRACT

A description of a method for the unambiguous synthesis of energetic oxetane ABA block copolymers is described. In this approach, a monofunctional hard block is allowed to react with a highly reactive diisocyanate in which the two isocyanates are of dramatically different reactivity. This forms an isocyanate capped hard block without significant dimerization. This isocyanate-terminated polymer is then allowed to condense with a difunctional soft block to form the desired ABA structure. The synthesis of monofunctional oxetane polymers will also be described.

INTRODUCTION

The first report¹ in the literature of the unambiguous synthesis of an oxetane containing block polymer by a direct polymerization method suggests the difficulties to be encountered in the preparation of these materials. Ample evidence exists from research into the preparation of energetic oxetane block polymers to suggest that similar difficulties are to be found with these materials also. A chemical linking of previously prepared telechelic homopolymers is an alternate approach to the synthesis of block polymers. This is the approach used^{2,3} to prepare oxetane-based (AB)_n block materials which are thermoplastic elastomers on a recent Ballistics Research Laboratory sponsored program into the use of these materials as LOVA binders. An obvious extension of this work was into the synthesis of ABA-type materials. This approach to ABA materials has the distinct advantage of utilizing a fully developed chemical strategy and proven analytical techniques. Any attempt to link difunctional A and B blocks and form exclusively ABA materials by controlling stoichiometry of the blocks is statistically unrealistic. To cleanly form an ABA thermoplastic elastomer material by a post polymerization linking, an absolutely monofunctional hard (A) block is needed. The preparation of monofunctional oxetane hard (A) block materials will lead directly to the unambiguous synthesis of ABA materials by a chemical linking with a difunctional soft (B) block.

RESULTS AND DISCUSSION

Early attempts to form a monofunctional energetic oxetane polymer by substitution of butanediol with butanol or a similar aliphatic alcohol in the standard boron trifluoride catalyzed polymerization^{4,5,6} failed to provide the desired 1.0 functional material with the necessary molecular weight control. An approach to this problem, suggested by work

*Approved for public release; distribution is unlimited.

performed on epichlorhydrin,⁷ was explored next. After our work was underway, a similar approach was reported to be effective in preparing a monofunctional polymer of 3-methyl-3-(trimethylsiloxyethyl)oxetane.⁸ This approach involves altering the mechanism from a polymerization involving a cation in the growing chain to the attack of a hydroxyl-terminated polymer on an activated monomer (Figure 1). This type of polymerization is

Standard Polymerization:



Activated Monomer Polymerization:

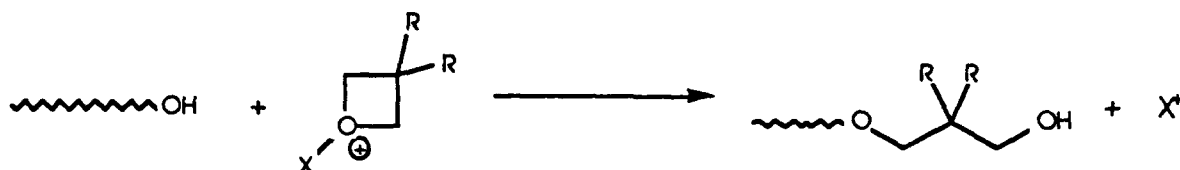


Figure 1. Depicted in this figure is the proposed mechanism for the propagation step of oxetane polymerization by the standard method and by the activated monomer method. The key difference is the activated monomer method involves attack of an alcohol on an activated monomer, which ensures rapid and complete initiator incorporation into the polymer chain.

obviously not a classical cationic. Several examples of this type of polymerization have been shown^{7,8} to approximate many of the characteristics of a living polymerization. To such a polymerization, the term "pseudo-living" is often applied. As a result of ongoing research with this system, reaction conditions have been developed that allow a controlled polymerization of energetic oxetanes with high initiator incorporation (which dictates functionality) and good molecular weight control. This has resulted in the production of true monofunctional energetic oxetane polymers. Besides monofunctional materials, di, tri and tetrafunctional materials are prepared with good control by this method (Figure 2). These data (Figure 2) are particularly significant because they show not only functionality control, but also the excellent molecular weight control attained. This degree of molecular weight control is necessary for the preparation of a series of block copolymers with controlled variation of total molecular weight and relative amounts of the individual blocks for mechanical property optimization and correlation to propellant properties.

The initiator system has been shown experimentally to exhibit the characteristics of an activated monomer "pseudo-living" polymerization mechanism mentioned above. This was shown by a series of classical tests of whether a polymerization is "living" involving the correlation of polymer properties and degree of conversion in the polymerization. These experiments illustrate the dramatic difference between oxetane polymerizations carried out using the activated monomer method and the earlier, standard method.^{4,5,6} In representative polymerizations to prepare difunctional 3,3-bis(azidomethyl)oxetane (BAMO) and 3,3-bis(ethoxymethyl)oxetane polymers using this activated monomer method and the earlier method, small aliquots were removed and quenched at several stages of the

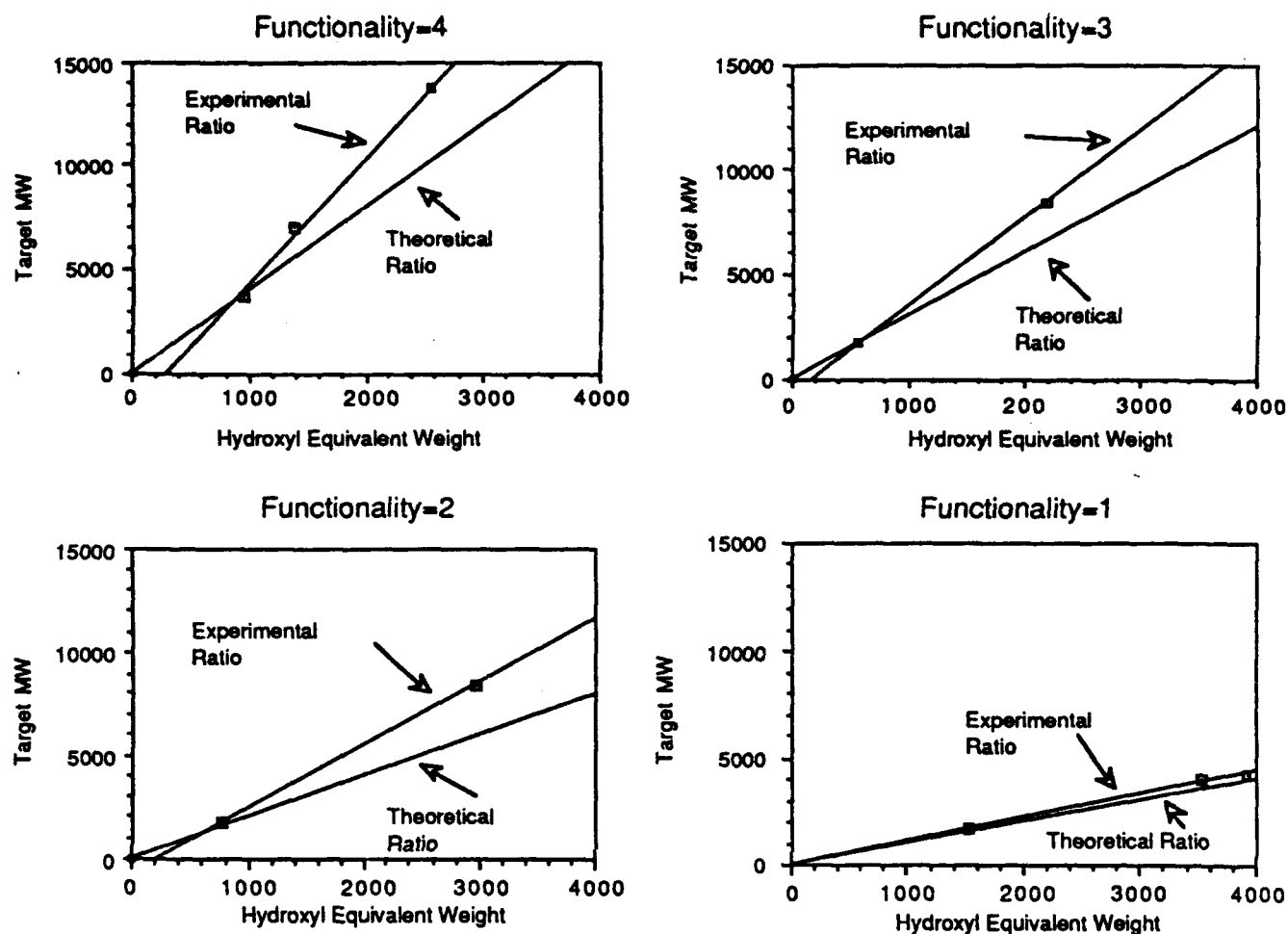


Figure 2. The series of graphs here details the success of the activated monomer polymerization at obtaining functionality and molecular weight control as evidenced by the close correlation of theoretical and experimental lines for molecular weight and experimental hydroxyl equivalent weight.

polymerization. The resulting polymers were analyzed,⁹ and the data gave a profile of the progression of the reaction (Figures 3 and 4). The molecular weight was shown to rise rapidly in the standard reaction and remain relatively constant throughout the polymerization typically with a small drop in the average molecular weight at high conversion. This drop in the molecular weight at the end of the reaction could be ascribed to attack of an active chain on an ether linkage of an existing polymer chain forming a tris(neoalkyl)oxonium ion which results in chain scission on quenching. Alternatively, monomer starvation at high conversion could make termination reactions other than that mentioned above kinetically more competitive with propagation reactions than early in the polymerization. This would result in the production of lower molecular weight polymer at high conversion than at low conversion and, thereby, lowering the total molecular weight near the end of the reaction. In contrast, the activated monomer polymerization showed a linear increase in molecular weight with conversion (Figures 3 and 4) with a Y-intercept near the origin. These are two classical characteristics of a "living" polymerization. Determination of the fate of the initial alcohol initiator charge also serves to highlight the differences in these two polymerizations. In the activated monomer polymerization, the initiator is incorporated into the polymer to a high degree

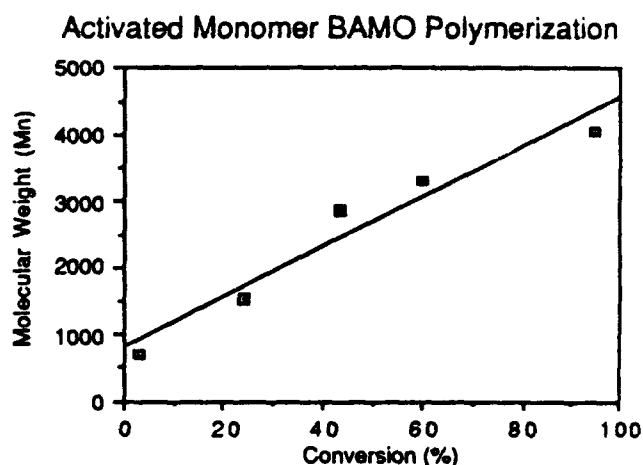
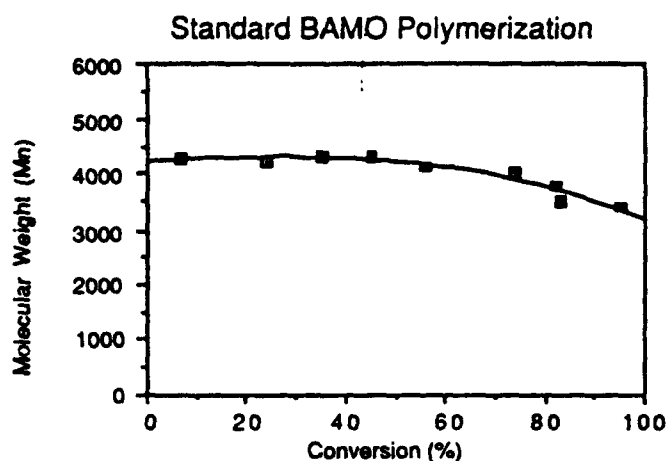


Figure 3. These two graphs illustrate the differences in the progress of BAMO polymerizations when carried out using the activated monomer method. The activated monomer method gives a linear increase in molecular weight with a Y-intercept near the origin, two key characteristics of a living polymerization.

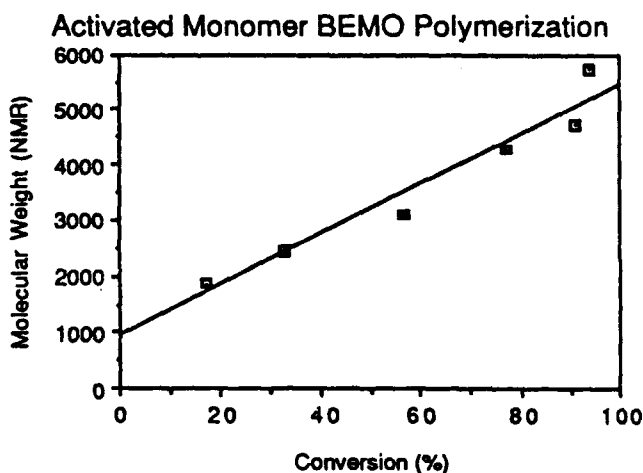
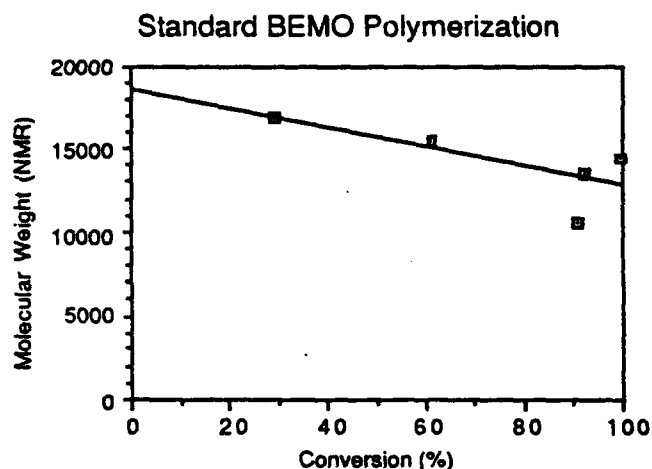


Figure 4. The two graphs above illustrate the difference in the progress of BEMO polymerizations when carried out using the activated monomer method. The activated monomer method gives a linear increase in molecular weight with a Y-intercept near the origin, two key characteristics of a living polymerization.

early in the reaction with the majority ultimately incorporated internally (i.e. both alcohol moieties of a butanediol have functioned as initiating sites). The standard^{4,5,6} polymerization resulted in a low degree of initiator incorporation (Figures 5 and 6). These data also support the claim that the modified activated monomer polymerization is "pseudo-living." Further support for the mechanisms proposed (Figure 1) is a reduction of oligomeric products in the modified polymerization relative to the standard polymerization. Similar data, not shown in the figures reproduced here, have been obtained for polymerizations involving 3,3-dimethyloxetane.

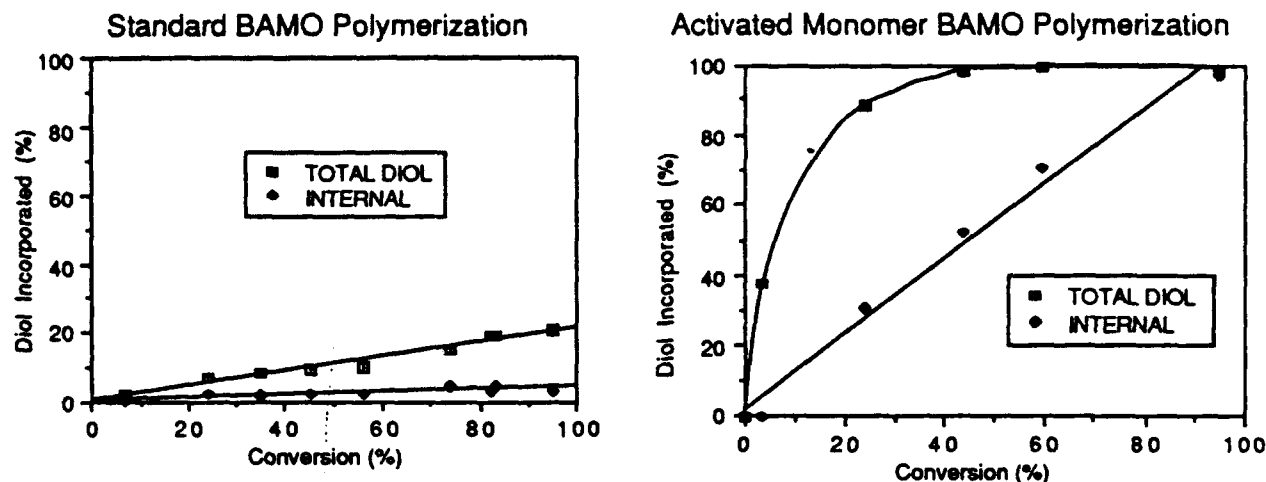


Figure 5. The two graphs above show the dramatic difference in the initiator incorporation for a BAMO polymer under the activated monomer reaction conditions. These data are in line with the mechanistic discussion and show the dramatic improvement made by this approach.

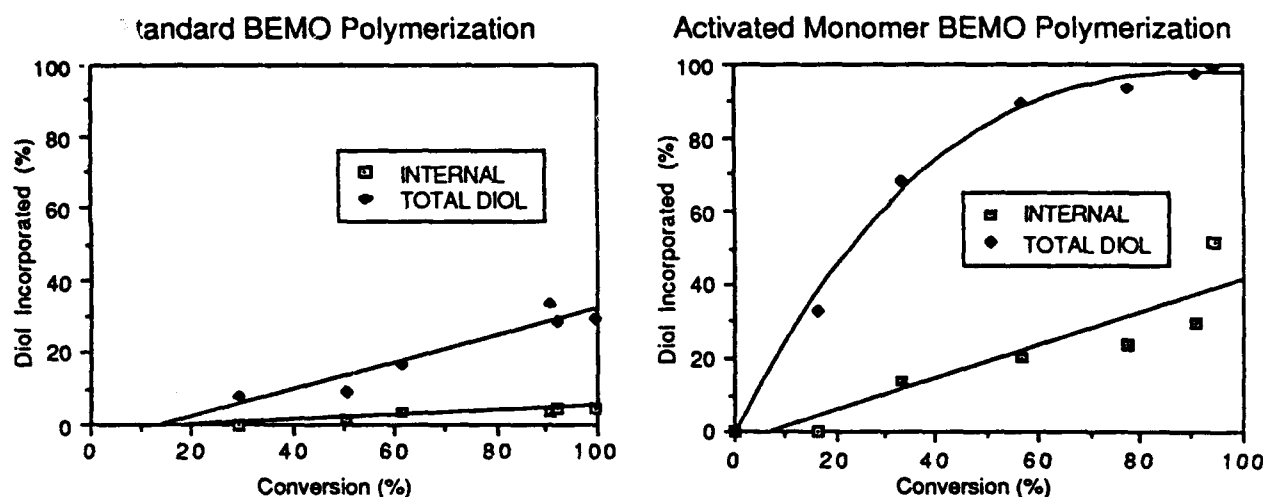


Figure 6. The two graphs show the dramatic difference in the initiator incorporation for a BEMO polymer under the activated monomer reaction conditions. These data are in line with the predictions based on the mechanistic discussion and show the dramatic improvement made by this approach.

These data from the step-growth polymerization suggested that the preparation of a bona fide oxetane ABA block copolymer by a sequential polymerization may in fact be possible using this "pseudo-living" polymerization. In a typical attempt to form an ABA block copolymer sequentially, a difunctional polymerization of 3-(azidomethyl)-3-methyloxetane (AMMO) was allowed to proceed to completion. At that time, a small aliquot of that reaction was removed and analyzed so that information on the intermediate AMMO homopolymer would be available for comparison to the final copolymer. A second charge of monomer was then added which, in this case, was BAMO. After the BAMO was polymerized the reaction was quenched and the product isolated. Using BAMO and AMMO monomers is particularly advantageous due to considerable data which has been generated on the analysis of resulting copolymers by ^{13}C and ^1H NMR.^{9,10,11,12} NMR methods alone are not sufficient to establish that a polymer has the desired ABA structure, however, they do provide information about several necessary conditions with a very rapid and simple

experiment. Data from a representative attempt at the preparation of an ABA material by this reaction are given in Table I.

TABLE I.
Representative Results from the Preparation of ABA Materials
by Sequential Polymerization^a

Sample Ref	Ratio (AMMO/BAMO)	GPC			NMR MW	Endgroups (AMMO/BAMO)	Block		Hydr Eq Wt
		Mw	Mn	Disp			Factor	Index	
7290	100/0	4.1	2.5	1.67	3.4	100/0	0	100	1689
7293	52/48	6.8	4.1	1.66	7.4	20/80	22	94	3247
Theory	50/50	--	--	--	7.4	0/100	21	92	3688

^aMw, Mn and NMR MW are given in thousands. The block factor is as has been defined¹⁰ which is the difference between the fraction of triads resulting from BAMO-BAMO-BAMO and BAMO-BAMO-AMMO, as measured by the fully relaxed ¹³C NMR of the quaternary carbons in the polymer, divided by 2. The block index is the sum of the integration of the absorbences of all BAMO-BAMO-BAMO triads and AMMO-AMMO-AMMO triads divided by the total number of triads. These data show the effective formation of a block material and that the second monomer was polymerized without an increase in polydispersity. However, the endgroup data shows that the material is not completely the desired ABA.

These data, the NMR portion of which will also be discussed elsewhere,¹¹ show that several necessary conditions were met in support of the ABA structure. The ¹H NMR spectrum most directly shows the deviation of the properties of the material obtained from that desired. The data in Table I are interpreted to require, if all the AMMO endgroups are assumed to be related to homopolymer, that only 80% of the product has the desired ABA architecture. Alternatively, if the assumption is made that all AMMO endgroups are related to a diblock material, then only 60% of the the product has the desired ABA structure with the remaining 40% being diblock. Most likely, chemical reality is somewhere in between, although the lack of an increase in polydispersity on polymerization of the second monomer relative to that obtained for the homopolymer suggests that the diblock structure is the predominate impurity. To date, the best efforts have provided slightly higher percentages of BAMO hydroxyl endgroups than those listed in Table I. The data indicate that, at best 85% of the product has the ABA arrangement (assuming homo AMMO as the other product). Although this percentage is relatively high and comparable to several commercial ABA materials, a less ambiguous route to high purity ABA material was sought. Therefore, attention returned to the original concept of the block linking of a monofunctional hard block to a difunctional (or higher functionality if a star configuration is desired) soft block.

With a 1.0 functionality material in hand, the preparation of an ABA material followed well preceded lines because the reaction could be performed in a fashion completely analogous to that used to prepare (AB)_n materials by a block linking approach.¹³ Generally, a monofunctional hard block, typically BAMO, is allowed to react with a slight molar excess of 2,4-toluenediisocyanate (2,4-TDI) in the presence of a catalytic amount of diphenyltin dichloride. The large differential reactivity of the two isocyanate functionalities, estimated at a factor of 26.6 when reacting with an unhindered alcohol,¹⁴ precludes any measurable dimerization reaction from occurring. The resulting isocyanate

terminated polymer is then allowed to react with a difunctional (or higher functionality) soft block such as AMMO or 3-methyl-3-(nitratomethyl)oxetane (NMMO). These soft blocks are particularly advantageous because the relatively high reactivity of the hydroxyl endgroups allows the condensation reaction with the less reactive isocyanate of 2,4-TDI to proceed at a reasonable rate. There is generally no need for a double capping followed by linking with an agent such as butanediol as was the case with most materials used to form the (AB)_n materials.^{2,3,12} The progress of the reaction is monitored by both 300 MHz ¹H NMR and FTIR.¹² These two analytical methods complement and corroborate each other well in this instance. The progress of the isocyanate plus alcohol reaction to afford urethane can be followed easily. In ¹H NMR spectra, the methylene adjacent to the terminal alcohol has a signal distinct from that same methylene when adjacent to a urethane linkage. These two absorbences can be quantified and compared. During the course of a reaction, the conversion of alcohol termini to urethane linkages can be followed. The carbonyl absorbences of the isocyanate moieties in 2,4-TDI and in the urethane resulting from the condensation of these functional groups with oxetane terminal alcohols are well-defined and strong in an FTIR spectrum, even at the low concentration present in this reaction. This allows, parallel to monitoring of the alcohol-to-urethane reaction by ¹H NMR, the observation by FTIR of the conversion of the isocyanate to urethane based on carbonyl absorbences. Together these methods provide strong evidence that the intended block linking reaction is proceeding as intended. Table II contains data obtained from the analysis of the product of a representative linking reaction.

TABLE II.
Representative Results from the Preparation of ABA Materials
by Block Linking^a.

Sample Ref	Ratio (AMMO/BAMO)	GPC			NMR		Endgroups		Block		Hydr
		Mw	Mn	Disp	MW		(AMMO/BAMO)	Factor	Index		Eg Wt
18670	100/0	12.4	6.0	2.06	7.3		100/0	0	100		3546
18671	0/100	5.7	3.1	1.85	3.2		0/100	50	100		3521
05712	60/40	15.5	8.1	1.92	12.6		6/94	20	100		--
Theory	60/40	- -	- -	- -	14.1		0/100	20	100		- -

^aAll data are as defined in Table I. The BAMO 'endgroups' in the final product are the initiating alcohol used to prepare the monofunctional BAMO hard block. These data show that the reaction proceeds without a significant increase in polydispersity. Determination of the hydroxyl equivalent weight in the product by a titration method was not possible due to interference with the test method by the -NH- moieties of the urethane linkages.

The GPC molecular weight increased significantly while the polydispersity of the product is intermediate between the two starting materials. This shows that the linking reaction was largely successful and that side reactions were not significant. The ¹H NMR molecular weight and endgroup type are both based on the observation that nearly all the terminal alcohol groups were converted to urethanes leaving the pendant chain of the alcohol used to initiate the monofunctional polymerization of BAMO as the major endgroup. In the case of a block linking reaction, the ¹³C NMR block data is somewhat trivial as the polymerizations were carried out separately so the existence of perfect block structure is to be expected. By this method, several materials have been prepared.

EXPERIMENTAL

^1H NMR spectra were recorded with a Varian XL-300 spectrometer operating at 300 MHz. ^{13}C NMR spectra were recorded with the same instrument operating at 75 MHz. Spectra were obtained on CDCl_3 solutions using residual CHCl_3 as internal standard. FTIR spectra were recorded with a Nicolet 20DX on dilute CH_2Cl_2 solutions. GPC traces were obtained with a waters LC for GPC using THF as the mobile phase and a differential refractometer detector. A series of four microstyragel columns was used ranging in porosity from 10^5 to 10^2 Å. Polyethyleneglycoladipate was used as a broad molecular weight calibration standard. Hydroxyl equivalent weight was determined by reaction with tosylisocyanate in THF followed by titration of the urethane with t-butylammonium hydroxide.

A typical block linking reaction serves to illustrate the method:

BAMO-AMMO-BAMO (notebook reference 05712). To a stirred solution of 4.0 g (1.24 mmol) of a monofunctional BAMO polymer in 8 ml of CH_2Cl_2 were added 0.193 ml (1.36 mmol) of 2,4-toluenediisocyanate and 0.004 g (0.012 mmol) of diphenyltin dichloride. After 18 hours, ^1H NMR analysis suggests a high percentage of alcohol endgroups had been converted to urethanes. FTIR shows strong isocyanate and urethane absorbences. To this solution were added 4.52 g (0.62 mmol) of a difunctional AMMO polymer in 10 ml of CH_2Cl_2 . After 45 hours more, FTIR shows no isocyanate absorbance. ^1H NMR shows that a high percentage of AMMO endgroups had reacted. The product was isolated by removal of all volatiles under reduced pressure.

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APPENDIX D

Improvements in the Producibility and Reproducibility
of Polyoxetane Prepolymers and Thermoplastic Elastomers

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INTRODUCTION:

An attractive approach to high energy propellants involves the use of energetic oxetane thermoplastic elastomers (TPEs). Theoretical performance calculations on energetic oxetanes using experimental heats of formation have shown an increase of greater than 15 lb-sec/lb relative to a PEG/HMX minimum smoke propellant when used in conjunction with a caged nitramine oxidizer. TPEs as a class of propellant binders are attractive from a processing point of view in terms of lower cost and increased safety. However, no viable oxetane TPE propellant binders have been prepared to date. Therefore, these projected payoffs have not been realized. Our approach to this problem is to investigate an alternative polymerization of energetic oxetanes that we have shown has distinct advantages over the methods currently used by others. This improved chemistry will allow the development of oxetane TPEs as viable propellant binders.

RESULTS AND DISCUSSION

The classical cationic polymerization of oxetanes has been actively investigated for over thirty years.^{1,2,3} In a program sponsored by BRL to investigate this type of polymerization to form oxetane block copolymer TPEs for use as LOVA binders at Thiokol, several shortcomings of this chemistry were discovered, including: lack of molecular weight control, lack of product reproducibility, poor initiator incorporation, and failure to adequately form block copolymers with the desired structure. Results from the SDIO/IST program on the preparation of oxetane ABA block copolymers have verified our findings.^{4,5,6,7} An approach to avoiding these problems was suggested by work from the open literature on the polymerization of cyclic ethers^{8,9} and by an understanding of the chemical basis for the problems. This approach involves altering the mechanism from a polymerization involving a cation in the growing chain to the attack of a hydroxyl-terminated polymer on an activated monomer (Figure 1). This method has several advantages, the most important of which is that it avoids the highly active, unstable cationic propagating species. This change will minimize the likelihood of the well documented^{1,3} intra- and intermolecular formation of a stable tris(neoalkyl)oxonium ion that serves as a termination reaction in the polymerization of 3,3-disubstituted oxetanes (Figure 2). The activated monomer polymerization uses only catalytic amounts of a stable acid catalyst and an inexpensive alcohol coinitiator and is run at or slightly above room temperature. In contrast, the classical cationic polymerization employs a stoichiometric silver-based catalyst and a marginally stable coinitiator and is run at -90°C.

As a result of ongoing research with the activated monomer approach at Thiokol, reaction conditions have been developed that allow a controlled polymerization of energetic oxetanes with high initiator incorporation (which dictates functionality) and good molecular weight control. Besides the standard difunctional polymers, mono, tri and tetrafunctional materials are prepared with good control by this method. Figure 3 shows the molecular weight control attained with this polymerization. This degree of molecular weight control is necessary for the

preparation of a series of block copolymers with controlled variation of total molecular weight and relative amounts of the individual blocks for mechanical property optimization and correlation to propellant properties. Using the activated monomer polymerization, reproducibility of a given set of properties is easily achieved (figure 4).

Standard Polymerization:



Activated Monomer Polymerization:

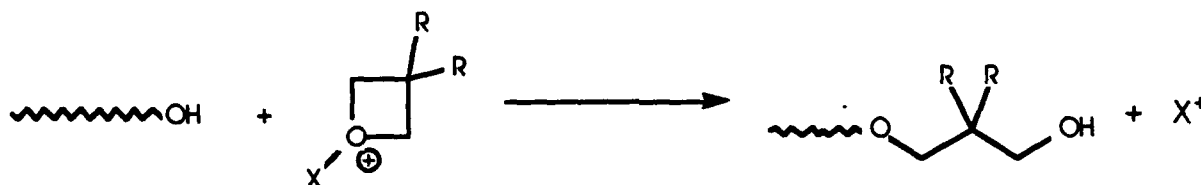
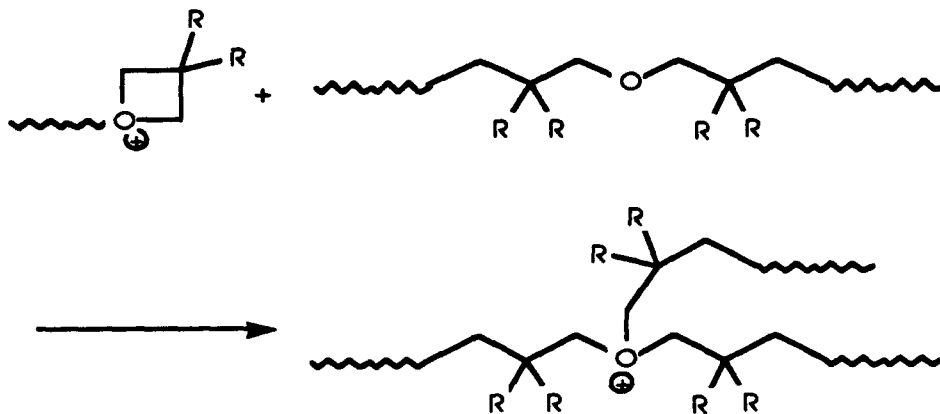


Figure 1. Depicted in this figure is the proposed mechanism for the propagation step of oxetane polymerization by the standard method and by the activated monomer method. The key difference is the activated monomer method involves attack of an alcohol on an activated monomer, which ensures rapid and complete initiator incorporation into the polymer chain.

The Thiokol initiator system has been shown experimentally to exhibit the characteristics of an activated monomer "pseudo-living" polymerization mechanism.^{8,9} This was shown by a series of classical tests of whether a polymerization is "living" involving the correlation of polymer properties and degree of conversion in the polymerization. These experiments illustrate the dramatic difference between oxetane polymerizations carried out using the activated monomer method and the earlier, standard method.^{10,11,12} In representative polymerizations to prepare difunctional 3,3-bis(azidomethyl)oxetane (BAMO) polymers using this activated monomer method and the earlier method, small aliquots were removed and quenched at several stages of the polymerization. The resulting polymers were analyzed,^{13,14} and the data gave a profile of the progression of the reaction (Figures 5). The molecular weight was shown to rise rapidly at the start of the standard reaction and remain relatively constant throughout the polymerization, typically with a small drop in the average molecular weight at high conversion. This drop in the molecular weight at the end of the reaction could be ascribed to attack of an active chain on an ether linkage of an existing polymer chain forming a tris(neoalkyl)oxonium ion which results in chain scission on quenching (Figure 2). Alternatively, monomer starvation at high conversion could make termination reactions other than that mentioned above kinetically more competitive with propagation reactions than early in the polymerization. This would result in the production of lower molecular weight polymer at high conversion than at low conversion and, thereby, lowering the average molecular weight near the end of the reaction. In contrast, the activated monomer polymerization showed a linear increase in molecular weight with conversion (Figures 5) and a Y-intercept near the origin. These are two characteristics of a "living" polymerization.

Intermolecular Formation of a Tris(neoalkyl)oxonium Ion:



Intramolecular Formation of a Tris(neoalkyl)oxonium Ion:

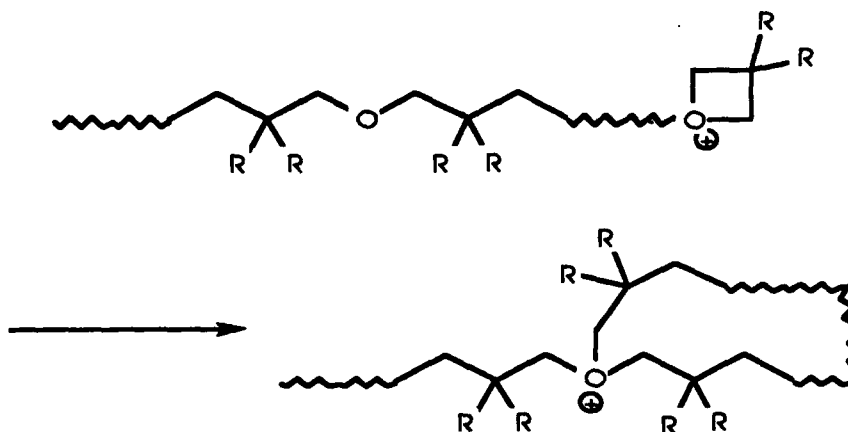


Figure 2. Depicted in this figure are the two routes to the formation of a highly stable tris(neoalkyl)oxonium ion. These are terminating reactions in the polymerization of 3,3-disubstituted oxetanes and, in the case of the intramolecular route, give rise to the formation of cyclic oligomers.

Determination of the fate of the initial alcohol initiator charge also serves to highlight the differences in these two polymerizations. In the activated monomer polymerization, the initiator is incorporated into the polymer to a high degree early in the reaction with the majority ultimately incorporated internally (i.e. both alcohol moieties of a butanediol have functioned as initiating sites). The standard^{10,11,12} polymerization resulted in a low degree of initiator incorporation (Figure 6). These data also support the claim that the modified activated monomer polymerization is "pseudo-living." Further support for the mechanisms proposed (Figure 1) is a reduction of oligomeric products in the modified polymerization relative to the standard polymerization. Similar data, not shown in the figures reproduced here, have been obtained for polymerizations involving 3,3-bis(ethoxymethyl)oxetane and 3,3-dimethyloxetane.

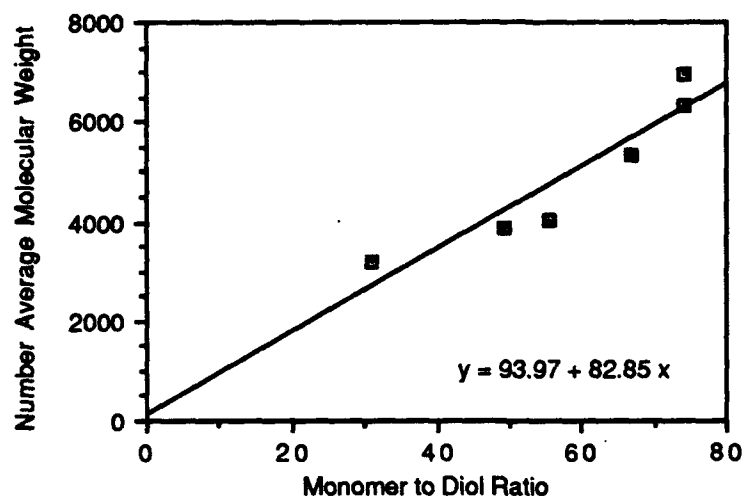


Figure 3. This graph details the success of the Thiokol activated monomer polymerization at obtaining molecular weight control as evidenced by the linearity of the data and the interception of the y-axis near the origin.

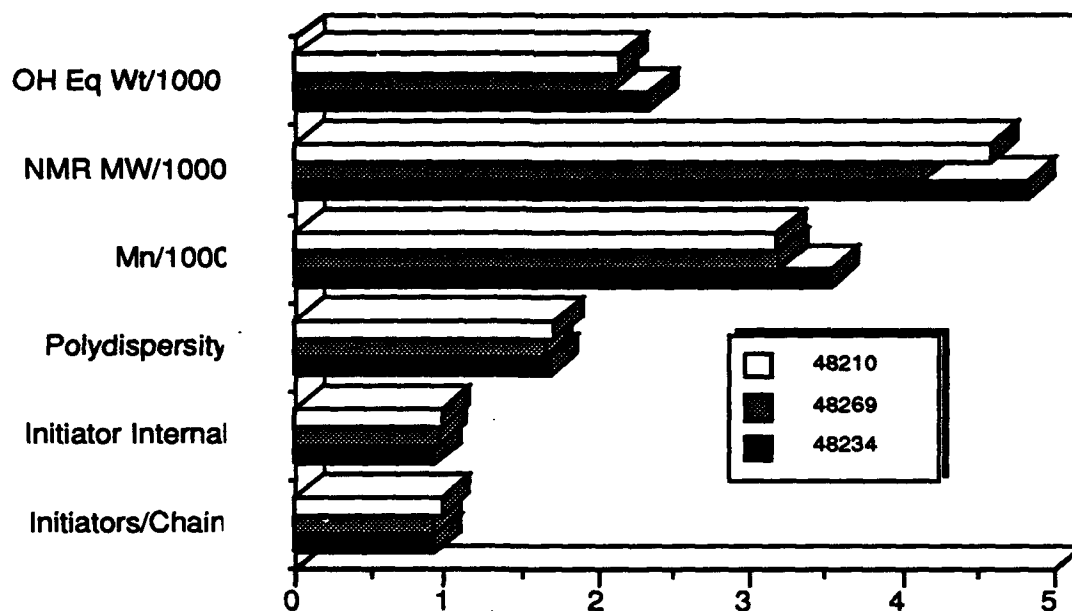


Figure 4. Shown here is the remarkable reproducibility of BAMO/NMMO polymer using the activated monomer polymerization. This reproducibility paves the way for serious propellant development.

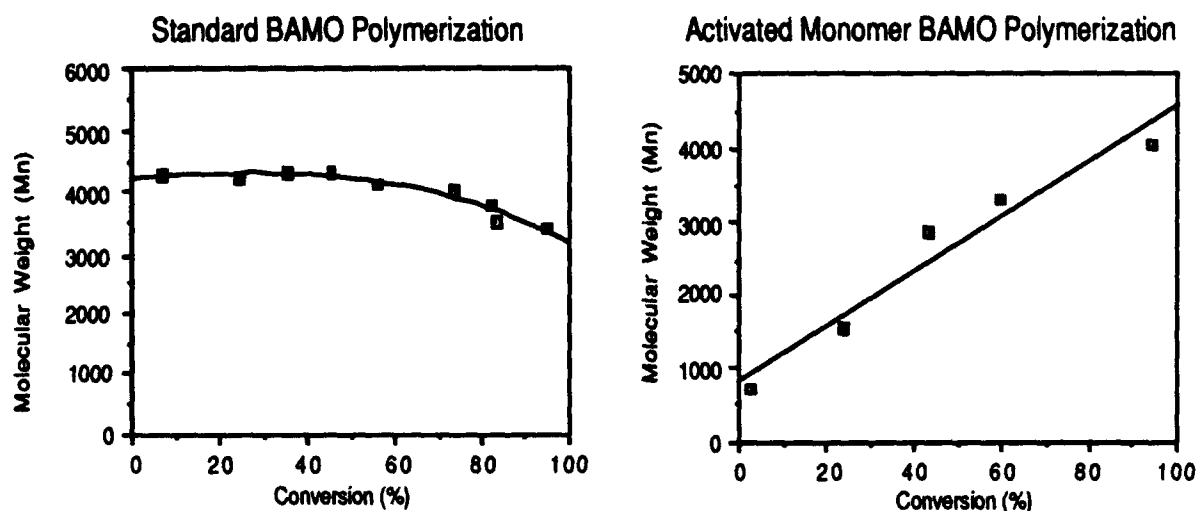


Figure 5. These two graphs illustrate the differences in the progress of BAMO polymerizations when carried out using the Thiokol activated monomer method. The activated monomer method gives a linear increase in molecular weight with a Y-intercept near the origin, two key characteristics of a living polymerization.

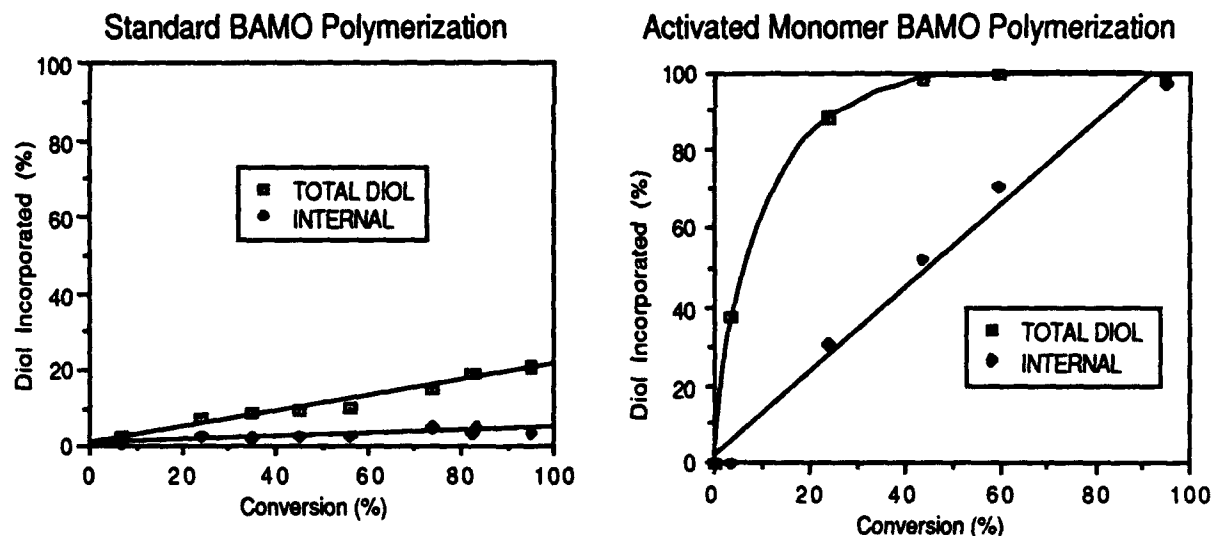


Figure 6. The two graphs above show the dramatic difference in the initiator incorporation for a BAMO polymer under the Thiokol activated monomer reaction conditions. These data are in line with the mechanistic discussion and show the dramatic improvement made by this approach.

These data from our activated monomer polymerization method suggested that the preparation of a bona fide oxetane ABA block copolymer by a sequential polymerization may in fact be possible using this "pseudo-living" polymerization. In a typical attempt to form an ABA block copolymer sequentially, a difunctional polymerization of 3-(azidomethyl)-3-methyloxetane (AMMO) was allowed to proceed to completion. At that time, a small aliquot of that reaction was removed and analyzed so that information on the intermediate AMMO homopolymer would be available for comparison to the final copolymer. A second charge of monomer was then added which, in this

case, was BAMO. After the BAMO was polymerized the reaction was quenched and the product isolated. Using BAMO and AMMO monomers is particularly advantageous due to considerable data which has been generated on the analysis of resulting copolymers by ^{13}C and ^1H NMR.^{13,15,16,17} NMR methods alone are not sufficient to establish that a polymer has the desired ABA structure, however, they do provide information about several necessary conditions with a very rapid and simple experiment. Data from a representative attempt at the preparation of an ABA material by this reaction are given in Table I. A similar material was submitted to NWC for their detailed analysis.⁷ Results from the GPC fractionation of that material are given in Figure 7.

TABLE I.
Representative Results from the Preparation of an ABA Material
by a Sequential Polymerization Using the Thiokol Activated Monomer Method^a

Sample	Ratio	GPC			NMR	Endgroups	Block		Hydr
Ref	(AMMO/BAMO)	Mw	Mn	Disp	MW	(AMMO/BAMO)	Factor	Index	Eq Wt
7290	100/0	4.1	2.5	1.67	3.4	100/0	0	100	1689
7293	52/48	6.8	4.1	1.66	7.4	20/80	22	94	3247
Theory	50/50	--	--	--	7.4	0/100	21	92	3688

^aMw, Mn and NMR MW are given in thousands. The block factor is as has been defined⁴ which is the difference between the fraction of triads resulting from BAMO-BAMO-BAMO and BAMO-BAMO-AMMO, as measured by the fully relaxed ^{13}C NMR of the quaternary carbons in the polymer, divided by 2. The block index is the sum of the integration of the absorbences of all BAMO-BAMO-BAMO triads and AMMO-AMMO-AMMO triads divided by the total number of triads. These data show the effective formation of a block material and that the second monomer was polymerized without an increase in polydispersity. The endgroup data shows that the material contains 60-80% of the desired ABA structure.

These data show that several necessary conditions were met in support of the ABA structure. The ^1H NMR spectrum most directly shows the deviation of the properties of the material obtained from that desired. The data in Table I are interpreted to require, if all the AMMO endgroups are assumed to be related to homopolymer, that 80% of the product has the desired ABA architecture. Alternatively, if the assumption is made that all AMMO endgroups are related to a diblock material, then only 60% of the the product has the desired ABA structure with the remaining 40% being diblock. Most likely, chemical reality is somewhere in between, although the lack of an increase in polydispersity on polymerization of the second monomer relative to that obtained for the homopolymer suggests that the diblock structure is the predominate impurity. The GPC fractionation data also support the theory that the diblock is the likely impurity. To date, the best efforts have provided slightly higher percentages of BAMO hydroxyl endgroups than those listed in Table I. The data indicate that, at best 85% of the product has the ABA arrangement (assuming homo AMMO as the other product). Although this percentage is relatively high and comparable to several commercial ABA materials, an unambiguous route to high purity ABA materials by a sequential polymerization is still under investigation.

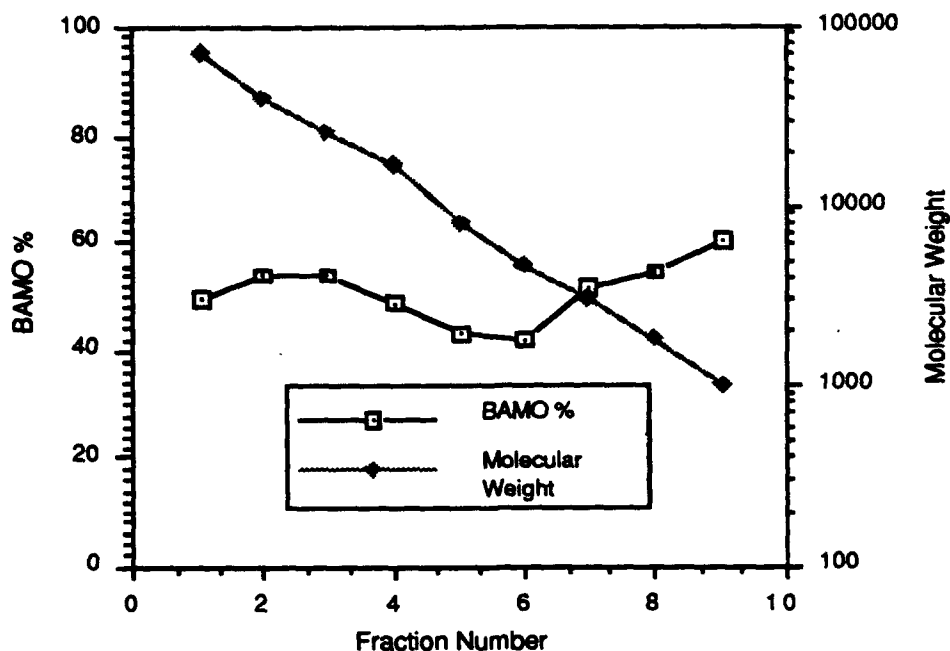


Figure 7. Reproduced here are the data obtained at NWC from quantitative GPC fractionation of a Thiokol activated monomer polymerized BAMO-AMMO-BAMO block copolymer. These results show a consistent percentage of BAMO throughout the entire molecular weight range of the polymer, suggesting good block copolymer formation.

CONCLUSIONS:

The activated monomer approach to the preparation of oxetane polymers results in good molecular weight and functionality control. The polymerization has many of the characteristics of a living polymerization and can be used to prepare materials with a relatively high percentage of ABA block structure as desired. These improvements will lead to the preparation of consistent, reproducible materials with improved properties as compared to previously prepared oxetane-based materials.

ACKNOWLEDGEMENTS:

The authors gratefully acknowledge the support received for this work from the U.S. Army Ballistics Research Laboratory, from the Office of Naval Research, and from Thiokol Independent Research and Development Funds.

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APPENDIX E

OXETANE THERMOPLASTIC ELASTOMERS FOR LOVA GUN PROPELLANT*

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INTRODUCTION

The results of Thiokol's completed High Energy-Low Vulnerability Ammunition (HE-LOVA) Propellant Development Program and several ongoing follow-on programs have demonstrated that energetic and non-energetic thermoplastic elastomers (TPEs) offer several advantages as the binder for Low Vulnerability Ammunition (LOVA) propellants. First, they can be processed thermally without a solvent like a thermoplastic. Second, upon cooling, TPEs have elastomeric properties that impart desirable mechanical properties to the propellant. Energetic TPEs also offer the possibility of improving ballistic performance without sacrificing vulnerability characteristics. The energy of a binder that is 50 percent 3,3-bis(azidomethyl)oxetane (BAMO) and 50 percent 3-azidomethyl-3-methyloxetane (AMMO) loaded at 76 percent with RDX is roughly 1300 joules per gram. This significantly exceeds any of the energy goals set to date for LOVA and is well above current gun propellants. Further, the energetic TPEs have an inherent higher burn rate than non-energetic TPEs. The high energy and high burn rate provide not only higher performance but allow room for a greater degree of freedom in formulating.

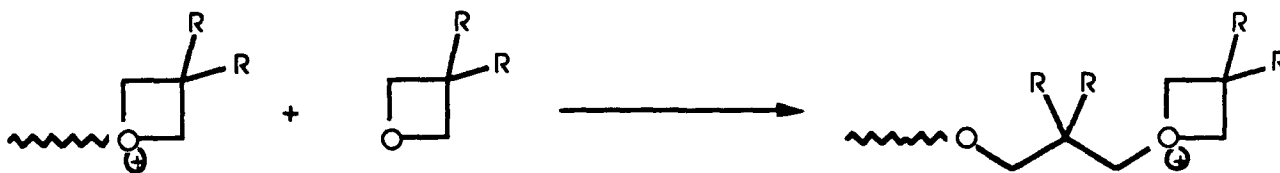
However, the synthesis of oxetane TPEs has been plagued with a lack of reproducibility and poor mechanical properties. Therefore, these projected payoffs have not been realized in any production system. Our approach to this mechanical property problem is to investigate an alternative polymerization of energetic oxetanes that we have shown has distinct advantages over the methods currently used by others. Linking of individually prepared blocks is also being examined. This improved chemistry will allow the development of oxetane TPEs as viable gun propellant binders.

RESULTS AND DISCUSSION

The classical cationic polymerization of energetic oxetanes has been actively investigated for several years.^{1,2,3} In a program sponsored by BRL to investigate oxetane TPEs as LOVA binders at Thiokol, several shortcomings of this chemistry were discovered⁴, including: lack of molecular weight control, lack of product reproducibility, poor initiator incorporation, and failure to adequately form block copolymers with the desired structure. Results from the SDIO/IST program on the preparation of oxetane ABA block copolymers have verified our findings.^{5,6,7,8} We have adopted an alternate polymerization. Using a non-catalytic amount⁹ of a highly active acid catalyst along with a molecular weight and functionality dictating amount of a polyol dramatically changes the polymerization of cyclic ethers such as oxetanes. The mechanism is changed from a polymerization involving a cation in the growing chain to the attack of a hydroxyl-terminated polymer on an activated monomer (Figure 1) and results in several dramatic improvements over the classical cationic polymerization of energetic oxetanes.^{10,11} Typically less than one-half of an equivalent of acid catalyst is used for each alcohol initiator functional group. We have found several catalysts to be active in this polymerization each with unique advantages. Among the acid catalysts of interest are: boron trifluoride etherate, triethoxonium tetrafluoroborate, fluorboric acid and the Sogah spiroxiloxane.¹² The activated monomer polymerization gives good molecular weight control, is reproducible, incorporates initiator well and provides block copolymers with chemical structures closer to the desired ABA structure (see Table I).

*Approved for public release; distribution is unlimited.

Standard Polymerization:



Activated Monomer Polymerization:

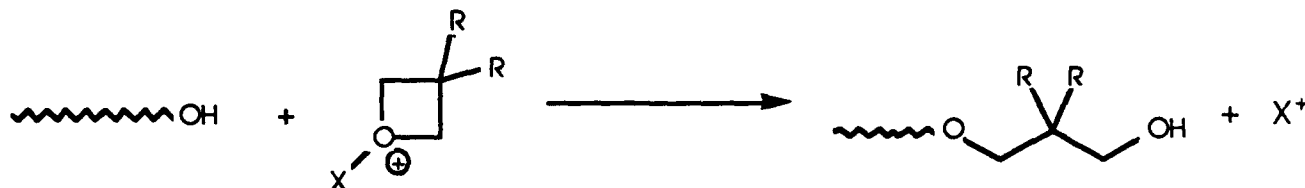


Figure 1. Depicted in this figure is the proposed mechanism for the propagation step of oxetane polymerization by the standard method and by the activated monomer method. The key difference is the activated monomer method involves attack of an alcohol on an activated monomer, which ensures rapid and complete initiator incorporation into the polymer chain.

TABLE Ia
Representative Results from the Preparation of ABA Materials
by Sequential Polymerization

Sample Ref	Ratio (AMMO/BAMO)	Mw	GPC Mn	Disp	NMR MW	Endgroups (AMMO/BAMO)	Block Factor	Index	Hydr Eq Wt
7290	100/0	4.1	2.5	1.67	3.4	100/0	0	100	1689
7293	52/48	6.8	4.1	1.66	7.4	20/80	22	94	3247
Theory	50/50	--	--	--	7.4	0/100	21	92	3688

^aMw, Mn and NMR MW are given in thousands. The block factor is as has been defined⁶ which is the difference between the fraction of triads resulting from BAMO-BAMO-BAMO and BAMO-BAMO-AMMO, as measured by the fully relaxed ¹³C NMR of the quaternary carbons in the polymer, divided by 2. The block index is the sum of the integration of the absorbances of all BAMO-BAMO-BAMO triads and AMMO-AMMO-AMMO triads divided by the total number of triads. These data show the effective formation of a block material and that the second monomer was polymerized without an increase in polydispersity. However, the endgroup data shows that the material is not completely the desired ABA.

While the data cited in Table I show the effectiveness of the activated monomer polymerization to prepare low molecular weight materials with good chemical properties, such a low molecular weight does not provide the desired mechanical properties. As the target molecular weight was increased, adventitious moisture became a more pronounced problem. Simple calculations show that twenty ppm of water in a high molecular weight polymerization (degree of polymerization >250) will provide as much initiator as the diol introduced into the reaction and make the resulting block copolymer less ABA-like. In the case of many non-energetic monomers, moisture is removed by distillation from reactive metal mirrors in closed systems. The monomers of interest to this effort are very energetic and

cannot be safely distilled. Further, the energetic functional groups (azide, nitrate ester) are not compatible with several of the common reagents used to dry monomers. Improvements in monomer purification during the last year have been made utilizing Schlenk vacuum techniques which has resulted in a further improvement in the polymerization characteristics particularly in the critical sequential polymerization to form ABA materials directly. Most important is the finding that lyophilization of monomers or intermediate prepolymers dissolved in benzene is a safe and effective way to remove moisture to the part per million level.

Two approaches were used to prepare oxetane ABA block copolymers without using any linking reagents. In the first approach, a difunctional polymerization of a soft block material such as 3-(azidomethyl)-3-methyloxetane (AMMO) was allowed to proceed to completion (see experimental section). The hard block monomer such as BAMO was then added. After the second monomer was polymerized, the reaction was quenched and the product isolated. This is a classical sequential polymerization of two monomers. The second approach used is a stepwise or restart method. In this alternative approach to forming an ABA polymer in a pseudo-sequential fashion, the homo- or random copolymer difunctional soft block was polymerized and isolated. This prepolymer with terminal alcohol functional groups was then used as a macromolecular initiator in the polymerization of the BAMO hard block. After the BAMO had polymerized, the block copolymer was isolated as in the case of the sequential polymerization. By these methods, materials were prepared with chemical purity similar to that cited in Table I.

By the sequential and restart approaches, twenty-four block copolymers were prepared. While several of these exhibited enough integrity to prepare samples for uniaxial mechanical property testing, only three of them, all restart polymerizations, were not too brittle or too soft to test accurately. Even in the three samples that were successfully tested, the mechanical properties were disappointingly poor (see Table II).

TABLE II^a
Mechanical Properties of ABA Block Copolymers
Prepared by Restart Polymerizations

<u>Lot</u>	<u>Soft Block</u>	<u>Modulus (psi)</u>	<u>Strain (%)</u>	<u>Stress (psi)</u>
129822	NMMO	642	12	32
129826	NMMO	355	9	25
129852	AMMO	146	24	19

^aStrain is true at maximum stress while stress is uncorrected.

Because of the very poor properties achieved by the sequential/restart approach, an alternate route to oxetane ABA materials was examined. Previously, ABA materials had been prepared in these laboratories using a 1.0 functionality hard block material by a block linking approach. Generally, a monofunctional hard block, in this case BAMO, is allowed to react with a slight molar excess of 2,4-toluenediisocyanate (2,4-TDI) in the presence of a catalytic amount of diphenyltin dichloride. The large differential reactivity of the two isocyanate functionalities, estimated at a factor of 26.6 when reacting with an unhindered alcohol,¹³ precludes any measurable dimerization reaction from occurring. The resulting isocyanate terminated polymer is then allowed to react with a difunctional soft block such as AMMO or 3-methyl-3-(nitratomethyl)oxetane (NMMO). These soft blocks are particularly advantageous because the relatively high reactivity of the hydroxyl endgroups allows the condensation reaction with the less reactive isocyanate of 2,4-TDI to proceed at a reasonable rate. There is generally no need for a double capping followed by linking with an agent such as butanediol as was the case with most materials used to form the (AB)_n materials.¹¹ The progress of the reaction is monitored by both 300 MHz ¹H NMR and FTIR. These two analytical methods complement and corroborate each other well in this instance. The progress of the isocyanate plus alcohol reaction to

afford urethane can be followed easily. In ^1H NMR spectra, the methylene adjacent to the terminal alcohol has a signal distinct from that same methylene when adjacent to a urethane linkage. These two absorbences can be quantified and compared. During the course of a reaction, the conversion of alcohol termini to urethane linkages can be followed. The carbonyl absorbences of the isocyanate moieties in 2,4-TDI and in the urethane resulting from the condensation of these functional groups with oxetane terminal alcohols are well-defined and strong in an FTIR spectrum, even at the low concentration present in this reaction. This allows, parallel to monitoring of the alcohol-to-urethane reaction by ^1H NMR, the observation by FTIR of the conversion of the isocyanate to urethane based on carbonyl absorbences. Together these methods provide strong evidence that the intended block linking reaction is proceeding as intended. Table III contains data obtained from the analysis of the product of a representative linking reaction.

TABLE III^a
Representative Results from the Preparation of ABA Materials
by Block Linking

Sample Ref	Ratio (AMMO/BAMO)	GPC Mw	GPC Mn	GPC Disp	NMR MW	Endgroups (AMMO/BAMO)	Block Factor	Block Index	Hydr Eq Wt
18670	100/0	12.4	6.0	2.06	7.3	100/0	0	100	3546
18671	0/100	5.7	3.1	1.85	3.2	0/100	50	100	3521
05712	60/40	15.5	8.1	1.92	12.6	6/94	20	100	--
Theory	60/40	--	--	--	14.1	0/100	20	100	--

^aAll data are as defined in Table I. The BAMO 'endgroups' in the final product are the initiating alcohol used to prepare the monofunctional BAMO hard block. These data show that the reaction proceeds without a significant increase in polydispersity. Determination of the hydroxyl equivalent weight in the product by a titration method was not possible due to interference with the test method by the -NH- moieties of the urethane linkages.

The GPC molecular weight increased significantly while the polydispersity of the product is intermediate between the two starting materials. This shows that the linking reaction was largely successful and that side reactions were not significant. The ^1H NMR molecular weight and endgroup type are both based on the observation that nearly all the terminal alcohol groups were converted to urethanes leaving the pendant chain of the alcohol used to initiate the monofunctional polymerization of BAMO as the major endgroup. In the case of a block linking reaction, the ^{13}C NMR block data is somewhat trivial as the polymerizations were carried out separately so the existence of perfect block structure is to be expected. By this method, 25 lots of material were prepared. Of these, sixteen exhibited measurable mechanical properties. These properties are reproduced in Table IV. These properties are an improvement over those obtained by the sequential or restart approaches but are not nearly as good as desired for this effort. Therefore, a decision was made to re-examine the (AB)_n block copolymers that were used on the previous effort but using energetic BAMO hard blocks rather than non-energetic hard blocks as done before.

Using the precedent (AB)_n block linking approach,¹¹ twenty-two lots of oxetane block copolymers have been prepared that exhibited good enough mechanical properties for accurate testing. Difunctional BAMO homopolymer was used as the hard block. Lots with AMMO homopolymer, BAMO/AMMO random copolymer, NMMO homopolymer, and BAMO/NMMO random copolymer as soft block were prepared. The materials with an AMMO soft block exhibited the best mechanical properties (Table V).

TABLE IV^a
Mechanical Properties of ABA Block Copolymers Prepared by Block Linking

<u>Lot</u>	<u>Soft Block</u>	<u>Modulus (psi)</u>	<u>Strain (%)</u>	<u>Stress (psi)</u>
141772	AMMO	9468	17	526
141774	AMMO	10458	15	567
141777	AMMO	10940	14	420
141778	NMMO	11137	17	637
141780	AMMO	8233	15	320
141781	BAMO/NMMO	8605	14	337
141789	AMMO	69	37	15
141790	AMMO	319	72	57
141791	NMMO	3988	17	187
129812	NMMO	140	17	9
129819	NMMO	1915	11	81
129823	BAMO/AMMO	1651	9	107
129830	BAMO/NMMO	2052	11	147
129831	AMMO	44	36	5
129832	BAMO/NMMO	3418	7	204
129833	AMMO	106	76	37

^aStrain is true at maximum stress while stress is uncorrected. They have better properties than the ABA restart materials but still have disappointing properties.

TABLE V^a
Mechanical Properties of (AB)_n Block Copolymers Prepared by Block Linking

<u>Lot</u>	<u>Soft Block</u>	<u>Modulus (psi)</u>	<u>Strain (%)</u>	<u>Stress (psi)</u>
129839	AMMO	76	64	18
129841	AMMO	86	282	71
129843	AMMO	187	74	46
129847	NMMO	235	33	36
129849	AMMO	149	228	74
129851	NMMO	77	18	9
129856	BAMO/AMMO	78	18	12
129857	BAMO/AMMO	422	12	43
129859	AMMO	101	189	62
129868	NMMO	346	60	48
129870	NMMO	650	29	68
129872	NMMO	33	24	3
129873	AMMO	195	67	41
129874	BAMO/AMMO	1510	15	178
129877	BAMO/NMMO	165	22	20
129879	BAMO/NMMO	690	38	89
116113	AMMO	170	65	44
116114	AMMO	290	306	117
116115	AMMO	260	138	75
116119	BAMO/NMMO	1690	10	138
116121	BAMO/NMMO	485	8	22
116122	BAMO/NMMO	1346	8	105

^aStrain is true at maximum stress while stress is uncorrected. These materials have dramatically improved properties and several are true elastomers because they exhibit greater than 100% recoverable strain.

Twelve of the lots of block copolymers prepared were selected for formulation into gun propellant. At the time of the preparation of this paper, the data from the first six lots were available. Prior to formulation into gun propellant, thermal properties of the block copolymers were determined by DSC. These data are reported in Table VI. These data were used to set mixing and extruding temperatures. The ABA-linking material exhibits a significantly higher melting point than the (AB)_n materials. The low melting point of the (AB)_n formulation using both AMMO and NMMO soft blocks suggests that this phenomenon is a result of the (AB)_n configuration.

Table VI^a
Thermal Properties of Block Copolymers

Lot	Soft Block	T _g (°C)	T _m (°C)	T _d (°C)
129831	AMMO	-40	80	260
129849	AMMO	-38	63	260
129859	AMMO	-40	59	260
129868	NMMO	-18	57	221
129870	NMMO	-20	58	222
129872	NMMO	-25	57	221

^aAll data were determined by DSC.

The propellant formulation was designed to be very simple for evaluation of a wide spectrum of materials and contained nothing more than 24 percent block copolymer and 76 percent RDX. The RDX was bimodal five and two micron in a weight ratio of five-to-two. The propellant was mixed on an 86-gram scale in a Haake R-40 torque rheometer then extruded into propellant grains. The compressive stress, strain, and modulus data were determined for each lot of propellant. The strain rate was approximately 100 percent per second. As can be seen in the data in Table VII, the strain values varied from about 20 to 35 percent with several modes of failure. The most attractive mode of failure is a simple pancaking of the sample. Several of the materials exhibited this mode of failure. The maximum stress values varied from slightly above 600 psi to over 2400. The compressive test used involves right cylinders of the propellant cut from nominal 0.25 inch diameter strands. At a length/diameter ratio of 1.5, these samples were compressed at a crosshead speed of 20 in/min at ambient temperature.

Also reported in Table VII is the ballistic data for these propellant lots. The burn rates were determined at average pressures of 11,000 psi and 26,000 psi in an oil-filled strand burner. As was predicted for these energetic polymers, the burn rates are inherently quite high.

Table VII^a
LOVA Propellant Characterization

Lot	Soft Block	Mechanical Properties			Burn Rate	
		Stress (psi)	Strain (%)	Failure	11 kpsi (in/sec)	22 kpsi (in/sec)
129831	AMMO	707	19.9	P,S	1.83	4.85
129849	AMMO	2345	34.5	B,S	1.70	4.75
129859	AMMO	1933	29.5	B,S	1.63	4.96
129868	NMMO	2407	28.3	P	1.70	4.69
129870	NMMO	2263	23.9	P,S	1.70	4.72
129872	NMMO	630	20.6	P	1.7	4.87

^aStrain is true at maximum stress while stress is uncorrected. The failure modes are: P=pancake, B=barrel, and S=split.

The thermal properties of the propellants were examined by DSC (Table VIII). The glass transition temperature is determined by the soft block used with the AMMO exhibiting a lower glass transition than the NMMO. The materials show melting points that correlate with the block copolymer melting points. Each material has a small (<100 J/g) endothermic reaction near 190°C as is expected with a much larger (>1200 J/g) exotherm above 235°C.

These analyses were conducted on thin sections of the extruded propellant composition. Each material was analyzed over two temperature ranges to define both the low temperature and elevated temperature behavior. Nominal 20-mg samples were encapsulated in the aluminum DSC pan for low temperature analysis from -100°C to +185°C at 10°C/minute under a nitrogen purge. The glass transition point was clear from an abrupt change in the heat capacity. The melting points were less clear and in two cases no clear melting point could be determined. For the elevated temperature behavior, 2- to 5-mg samples were analyzed in the same manner except over the temperature range of ambient to 450°C. The small sample size was necessitated due to the magnitude of the exotherm. Both exothermic and endothermic reactions were noted. Because of the small sample size, the energy per unit weight is inherently less accurate than it would be with larger sample size.

Table VIII^a
Thermal Properties of LOVA Extruded Propellants

Lot	Soft Block	T _g (°C)	T _m (°C)	Endotherm		Exotherm	
				Peak (°C)	ΔH (J/g)	Peak (°C)	ΔH (J/g)
129831	AMMO	-43	82	188	96	239	1562
129849	AMMO	-41	46	188	89	237	1437
129859	AMMO	-41	—	188	94	237	1364
129868	NMMO	-20	44	187	85	239	1467
129870	NMMO	-35	—	188	91	239	1653
129872	NMMO	-25	58	187	89	240	1261

^aAll data were determined by DSC.

The propellant samples have been examined for selected temperature mechanical properties by the application of a static force on a cylindrical sample at 63°C. These analyses were conducted on right circular cylinders nominally 6 mm diameter and 5 mm length. The initial compression under a 5 psi load is measured with the samples exhibiting from 1.7 to 9.0 percent compression (Table IX). The longer term compression of the samples varied from 0.3 to 5.6 percent at one hour. The highest melting sample, as measured by DSC, showed the lowest compression and slump at 63°C. The initial compression for the other five propellant samples correlates directly with the maximum stress of the samples.

Table IX^a
Compression and Slump Test of LOVA Propellant at 63°C

Lot	Soft Block	Initial Compression (%)	60 min slump (%)
129831	AMMO	1.7	0.3
129849	AMMO	3.2	5.6
129859	AMMO	3.1	5.6
129868	NMMO	2.7	4.6
129870	NMMO	3.0	3.8
129872	NMMO	9.0	2.6

^aAll data were determined by thermomechanical analyzer measurements.

CONCLUSIONS

The oxetane block copolymers prepared exhibit some attractive properties in 76% solids LOVA gun propellant formulations. Improvements are needed in the 63°C compression and slump properties. This is being addressed by increasing the molecular weight of the BAMO hard block in future samples. Of the soft block materials tested to date, AMMO provides the best mechanical properties. The energy of the oxetane block copolymers is evident in the inherently high burn rates of the derived propellants. Further data will be reported on the rest of the samples to be evaluated on this program including scale-up efforts for larger propellant tests.

ACKNOWLEDGEMENTS

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APPENDIX F

Polyoxetane Thermoplastic Elastomers as Gun Propellant Binders

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INTRODUCTION:

An attractive approach to high energy propellants involves the use of energetic oxetane thermoplastic elastomers (TPEs). Theoretical performance calculations on energetic oxetanes using experimentally determined heats of formation have shown a predicted increase of 8 lb-sec/lb relative to a PEG baseline in a minimum smoke propellant and no loss in Isp while dropping from 91% solids to 75% solids in an AP/Al formulation by replacing HTPB. TPEs as a class of propellant binders are attractive from a processing point of view in terms of lower cost, increased safety, and ease of reclamation. However, no viable oxetane TPE propellant binders have been prepared to date and, in fact, no firm reports exist of any oxetane block polymers that meet the strict technical definition of a TPE (thermally processible with greater than 100% recoverable strain). Therefore, these projected payoffs have not been realized. Our approach to this problem is to investigate an alternative polymerization of energetic oxetanes that we have shown has distinct advantages over the methods currently used by others. This chemistry will serve as the basis for a sequential polymerization to form ABA block copolymers and for isocyanate linking to form ABA or (AB)_n block copolymers. This improved chemistry will allow the attainment of the goal to develop a viable oxetane propellant binder.

RESULTS AND DISCUSSION:

In a previous report to this group,¹ our efforts to improve the producibility and reproducibility of the polymerization of energetic oxetanes were described. The classical cationic polymerization of energetic oxetanes has been actively investigated for several years.^{2,3,4} In a program sponsored by BRL to investigate oxetane TPEs as gun propellant binders at Thiokol, several shortcomings of this chemistry were discovered,⁵ including: lack of molecular weight control, lack of product reproducibility, poor initiator incorporation, and failure to adequately form block copolymers with the desired structure. Results from the SDIO/IST program on the preparation of oxetane ABA block copolymers have verified our findings.^{6,7,8} We have adopted an alternate polymerization. Using a non-stoichiometric amount⁹ of a highly active acid catalyst along with a molecular weight and functionality dictating amount of a polyol dramatically changes the polymerization of cyclic ethers such as oxetanes. The mechanism is changed from a polymerization involving a cation in the growing chain to the attack of a hydroxyl-terminated polymer on an activated monomer and results in several dramatic improvements over the classical cationic polymerization of energetic oxetanes.¹⁰ Typically less than one-half of an equivalent of acid catalyst is used for each alcohol initiator functional group. We have found several catalysts to be active in this polymerization each with unique advantages. Among the acid catalysts of interest are: boron trifluoride etherate, triethoxonium tetrafluoroborate, fluorboric acid and the Sogah spiro-siloxane. The activated monomer polymerization gives good molecular weight control, is reproducible, incorporates initiator well and provides block copolymers with chemical structures closer to the desired ABA structure.

A series of oxetane ABA block copolymers were prepared with controlled properties (e.g. molecular weight, percent hard block) then structurally characterized. The emphasis is placed

on a thorough understanding of the chemical roots of the physical characteristics of the polymer so that modifications to the chemistry are made that will result in significant improvements in the polymer. A lack of this understanding would lead to confusion and ineffective research. The catalyst work has centered on two catalysts ($\text{BF}_3\text{-OEt}$ and Et_3OBF_4). Modifications have been made in the polymerization guided by the results from the analysis of the polymers. Unfortunately the best sequentially prepared ABA materials have failed to produce a product with attractive mechanical properties, therefore, an alternate approach to an oxetane TPE was sought.

Our current approach to improve mechanical properties is to prepare separate blocks and link them with isocyanates to form ABA or (AB) $_n$ materials that have higher total molecular weight than could be achieved by sequential polymerization. The mechanical properties obtained are a significant improvement over previous materials (see Table I) and so the majority of current effort is centered in this area. The best data we have suggests that a gumstock should be rather low modulus with a high recoverable strain number and reasonable but not necessarily high stress to ultimately yield a "good" propellant. These materials seem to come closer to these desirable properties and away from the tough (higher modulus) leathery materials made in the past that have not shown good propellant properties.

TABLE I
Representative Mechanical Properties Obtained from Oxetane Block Copolymers^a

Type	Elastomer	Modulus (psi)	Strain (%)	Stress (psi)
ABA-seq	AMMO	642	12	32
ABA-seq	NMMO	355	9	25
ABA-seq	AMMO	146	24	19
ABA-link	AMMO	69	37	15
ABA-link	AMMO	319	72	57
ABA-link	NMMO	3988	17	187
ABA-link	AMMO	44	36	5
(AB) $_n$	AMMO	86	282	71
(AB) $_n$	AMMO	149	228	74
(AB) $_n$	AMMO	101	189	62
(AB) $_n$	NMMO	346	60	48
(AB) $_n$	NMMO	650	29	68
(AB) $_n$	NMMO	33	24	3
(AB) $_n$	AMMO	170	65	44
(AB) $_n$	AMMO	290	306	117
(AB) $_n$	AMMO	260	138	75
(AB) $_n$	BAMO/NMMO	1690	10	138
(AB) $_n$	BAMO/NMMO	485	8	22
(AB) $_n$	BAMO/NMMO	1346	8	105

^aType refers to the method of preparation of the block copolymer. Elastomer is the soft block material that was used. In all cases, BAMO was the hard block. Strain is true and uncorrected at maximum stress and stress is uncorrected. The dramatic improvement of the (AB) $_n$ materials (except the BAMO/NMMO-based materials) is apparent.

This chemical linking of previously prepared telechelic homopolymers is the same approach used¹¹ to prepare oxetane-based (AB) $_n$ block materials which are thermoplastic elastomers on a previous Ballistics Research Laboratory sponsored program into the use of these oxetane copolymers as gun propellant binders. Besides preparation of (AB) $_n$ materials, an obvious

extension of this work was an examination of the synthesis of ABA-type materials. This approach to ABA materials has the distinct advantage of utilizing a fully developed chemical strategy and proven analytical techniques. Any attempt to link difunctional A and B blocks and form exclusively ABA materials by controlling stoichiometry of the blocks is statistically unrealistic. To cleanly form an ABA thermoplastic elastomer material by a post polymerization linking, an absolutely monofunctional hard (A) block is needed. Our activated monomer polymerization has made monofunctional oxetane hard (A) block materials available and led directly to the unambiguous synthesis of ABA materials by a chemical linking with a difunctional soft (B) block. The preparation of an ABA material followed well preceded lines because the reaction could be performed in a fashion completely analogous to that used previously to prepare (AB)_n materials by a block linking approach.¹² By this method, several materials have been prepared, although the (AB)_n materials have exhibited superior mechanical properties. Further evidence of the effectiveness of the linking reaction is given in figure 1. This figure shows data generated at NAWC by a GPC fractionation of an (AB)_n material. The even percentage of BAMO content across the molecular weight range shows that a high percentage of the desired linking reactions took place.

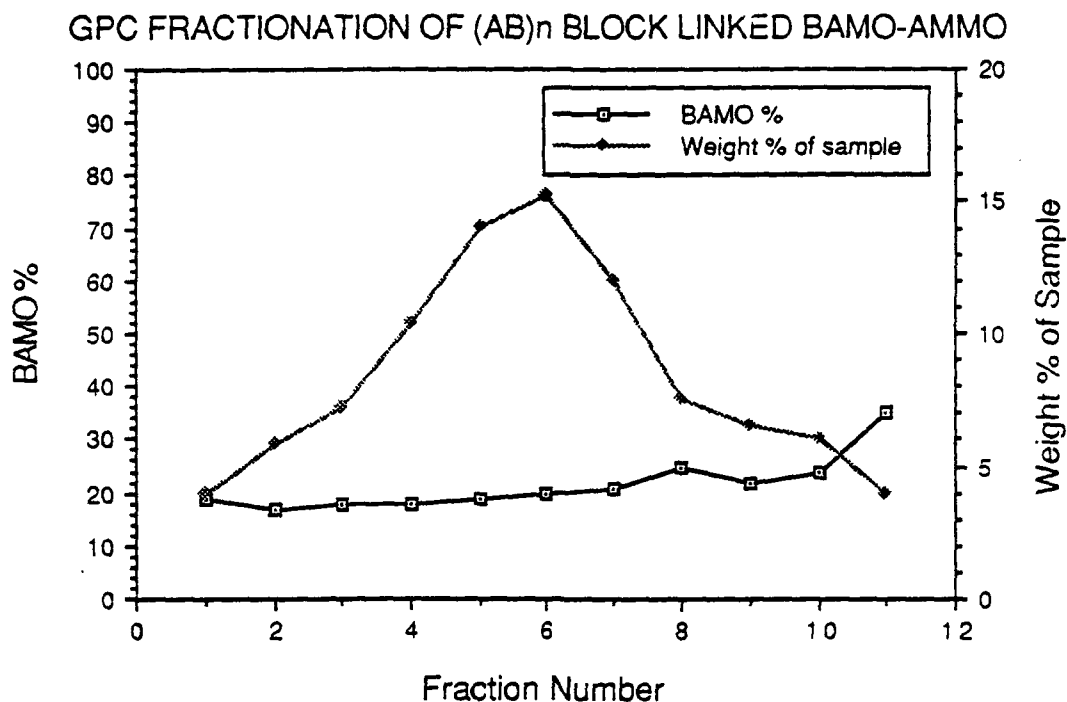


Figure 1. Reproduced here are the data obtained at NAWC from quantitative GPC fractionation of a Thiokol (AB)_n block linked BAMO-AMMO copolymer. These results show a consistent percentage of BAMO throughout the entire molecular weight range of the polymer, suggesting good block copolymer formation.

Twelve of the lots of block copolymers prepared were selected for formulation into gun propellant. Prior to formulation into gun propellant, thermal properties of the block copolymers were determined by DSC. These data are reported in Table II. These data were used to set mixing and extruding temperatures. The ABA-linking material exhibits the highest melting point. The low melting point of the (AB)_n formulation using both AMMO and NMMO soft blocks suggests that this phenomenon is a result of the (AB)_n configuration. The BAMO/NMMO materials have higher melting points perhaps due to the higher overall BAMO content leading to more complete crystallization of the hard block.

Table II
Thermal Properties of Block Copolymers^a

<u>Type</u>	<u>Soft Block</u>	<u>T_g (°C)</u>	<u>T_m (°C)</u>	<u>T_d (°C)</u>
ABA-link	AMMO	-40	80	260
(AB)n	AMMO	-38	63	260
(AB)n	AMMO	-40	59	260
(AB)n	NMMO	-18	57	221
(AB)n	NMMO	-20	58	222
(AB)n	NMMO	-25	57	221
(AB)n	AMMO	-45	55	255
(AB)n	AMMO	-43	61	255
(AB)n	AMMO	-43	67	256
(AB)n	BAMO/NMMO	-30	70	220, 247
(AB)n	BAMO/NMMO	-30	67	218, 245
(AB)n	BAMO/NMMO	-28	75	219, 246

^aAll data were determined by DSC.

The propellant formulation was designed to be very simple for evaluation of a wide spectrum of materials and contained nothing more than block copolymer and RDX. The RDX was bimodal five and two micron in a weight ratio of five-to-two. The propellant was mixed on an 86-gram scale in a Haake R-40 torque rheometer then extruded into propellant grains. The compressive stress, strain, and modulus data were determined for each lot of propellant. The strain rate was approximately 100 percent per second. As can be seen in the data in Table III, the strain values varied from near 20 to 35 percent with several modes of failure. The most attractive mode of failure is a simple pancaking of the sample. Several of the materials exhibited this mode of failure. The maximum stress values varied from slightly above 600 psi to over 2400. The compressive test used involves right cylinders of the propellant cut from nominal 0.25 inch diameter strands which were cut to a 1.5 length/diameter ratio.

Also reported in Table III is the burn rate data for these propellant lots. The burn rates were determined at average pressures of 11,000 psi and 26,000 psi in an oil-filled strand burner. As was predicted for these energetic polymers, the burn rates are inherently quite high.

The thermal properties of the propellants were examined by DSC (Table IV). The glass transition temperature is determined by the soft block used with the AMMO exhibiting a lower glass transition than the NMMO or BAMO/NMMO. The materials show melting points that correlate with the block copolymer melting points. Each material has a small (<100 J/g) endothermic reaction near 190°C as is expected with a much larger (>1200 J/g) exotherm above 235°C.

These analyses were conducted on thin sections of the extruded propellant composition. Each material was analyzed over two temperature ranges to define both the low temperature and elevated temperature behavior. Nominal 20-mg samples were encapsulated in the aluminum DSC pan for low temperature analysis from -100°C to +185°C at 10°C/minute under a nitrogen purge. The glass transition point was clear from an abrupt change in the heat capacity. The melting points were less clear and in two cases no clear melting point could be determined. For the elevated temperature behavior, 2- to 5-mg samples were analyzed in the same manner except over the temperature range of ambient to 450°C. The small sample size was necessitated due to the magnitude of the exotherm. Both exothermic and endothermic reactions were noted. Because of the small sample size, the energy per unit weight is inherently less accurate than it would be with larger sample size.

Table III
Oxetane TPE Propellant Characterization^a

Type	Soft Block	Mechanical Properties			Burn Rate	
		Stress (psi)	Strain (%)	Failure	11 kpsi (in/sec)	22 kpsi (in/sec)
ABA-link	AMMO	707	19.9	P,S	1.83	4.85
(AB)n	AMMO	2345	34.5	B,S	1.70	4.75
(AB)n	AMMO	1933	29.5	B,S	1.63	4.96
(AB)n	NMMO	2407	28.3	P	1.70	4.69
(AB)n	NMMO	2263	23.9	P,S	1.70	4.72
(AB)n	NMMO	630	20.6	P	1.77	4.87
(AB)n	AMMO	1090	29.9	P,S	1.51	4.23
(AB)n	AMMO	1370	29.3	P,S	1.52	4.37
(AB)n	AMMO	1350	27.3	P,S	1.53	4.36
(AB)n	BAMO/NMMO	992	17.6	P,S	2.04	5.13
(AB)n	BAMO/NMMO	627	16.5	P,S	2.10	5.26
(AB)n	BAMO/NMMO	1060	21.2	P,S	2.07	5.26

^aStrain is true at maximum stress while stress is uncorrected. The failure modes are:
P=pancake, B=barrel, and S=split.

Table IV
Thermal Properties of Oxetane TPE Extruded Propellants^a

Type	Soft Block	T _g (°C)	T _m (°C)	Endotherm		Exotherm	
				Peak (°C)	ΔH (J/g)	Peak (°C)	ΔH (J/g)
ABA-link	AMMO	-43	82	188	96	239	1562
(AB)n	AMMO	-41	46	188	89	237	1437
(AB)n	AMMO	-41	--	188	94	237	1364
(AB)n	NMMO	-20	44	187	85	239	1467
(AB)n	NMMO	-35	--	188	91	239	1653
(AB)n	NMMO	-25	58	187	89	240	1261
(AB)n	AMMO	-49	63	189	88	238	1155
(AB)n	AMMO	-44	55	190	98	240	1429
(AB)n	AMMO	-46	62	190	103	239	1319
(AB)n	BAMO/NMMO	-28	69	190	89	240	1738
(AB)n	BAMO/NMMO	-29	71	190	99	240	1675
(AB)n	BAMO/NMMO	-27	79	190	90	240	1677

^aAll data were determined by DSC.

CONCLUSIONS:

The oxetane block copolymers prepared exhibit attractive properties in gun propellant formulations. Of the soft block materials tested to date, AMMO provides the best mechanical properties. The energy of the oxetane block copolymers is evident in the inherently high burn rates of the derived propellants. Further data will be reported on this program including scale-up efforts for larger propellant tests and safety testing on the propellants made with the larger polymer samples.

ACKNOWLEDGEMENTS:

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